



HAL
open science

Field and electron beam-induced luminescence phenomena in polypropylene thin films

Bo Qiao, Gilbert Teyssedre, Christian Laurent

► **To cite this version:**

Bo Qiao, Gilbert Teyssedre, Christian Laurent. Field and electron beam-induced luminescence phenomena in polypropylene thin films. 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM'15), Jul 2015, Sydney, Australia. pp.196-199, 10.1109/ICPADM.2015.7295242 . hal-03943777

HAL Id: hal-03943777

<https://hal.science/hal-03943777>

Submitted on 19 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Field and Electron Beam-Induced Luminescence Phenomena in Polypropylene Thin Films

Bo Qiao, Gilbert Teyssedre and Christian Laurent

Laboratoire Plasma et Conversion d'Énergie

University of Toulouse & CNRS

Toulouse, France

gilbert.teyssedre@laplace.univ-tlse.fr

Abstract— Field-induced luminescence of insulating polymers is an exciting field of research. Being intrinsically related with the high-field electronic properties of the material, it provides a way to investigate electrical ageing and breakdown processes. It is particularly suited for those materials used in high field applications, e.g. thin films of polypropylene in capacitors. One of the puzzling aspects of electroluminescence in wide band gap polymers is that the emission spectra are only reproduced under electron beam irradiation. In this communication, we report for the first time the field and electron beam induced luminescence in polypropylene films. Measurements were performed on 17 μm -thick bi-oriented polypropylene films. The home-designed electron gun provides electrons of up to 10 keV in energies. Emission spectra acquired for different beam energies are compared to the electroluminescence spectra obtained under AC stress for fields in the range 150-300 kV/mm. The nature of the excitation process in field and electron beam-induced luminescence is discussed together with the nature of emitting species and their significance for ageing study.

Keywords— polypropylene thin film, electrical ageing, breakdown, electroluminescence, cathodoluminescence.

I. INTRODUCTION

Insulating polymeric materials are used in a large variety of applications in electrical engineering either as bulk insulation or in thin films form, e.g. high-voltage insulated cables, windings of coils for motors, generators, transformers, capacitors, etc. They provide very good insulating solutions but are subjected to deterioration in service under the influence of electrical and thermal stresses and others depending on the working environment (e.g. irradiation, mechanical, etc.). Their use in practical applications is therefore limited by their lifetime under a given stress and not so much by their intrinsic properties. One of the main threats for the insulation is the existence of partial discharges (PD) eroding the polymer. Solutions have been implemented to strengthen the insulation against PD when they are unavoidable (e.g. large generators, motors, etc.). However, practical situations exist where the existence of PDs has to be absolutely avoided, e.g. extra-high voltage cables with synthetic insulation, capacitors, etc. Moreover, the trend towards more compact electrical systems and electrical components with higher energy density involves pushing the limit in terms of electric field in the insulation. There is therefore a renewed interest in the electronic properties of insulating polymers. One of the key challenges in

investigating the electronic properties of insulating materials is to relate the basic transport mechanisms with critical transport regime where deterioration can occur, e.g. onset of hot electrons generation able to break atomic bonds and to generate defects. Detecting the optical emission from the investigated material under electric field provides a way to couple transport and dissipative processes through a possible signature of deleterious reactions at the atomic level.

Field-induced luminescence (or electroluminescence EL) of insulating polymers has been reported in a variety of materials for many years starting year 1967 [1] where the first consistent experiments were performed on films of polyethylene, polyethylene terephthalate, etc. In spite of a firm scientific activity along the time, emission spectra were sparsely reported and when they were, large band gap optical filters were used preventing the identification of the emitting species and therefore the underlying relaxation mechanisms. Only quite recently the possibility exists to acquire wavelength-resolved spectra of EL owing to the use of specialized Charge Coupled Device –CCD, coupled with an optical dispersive system [2, 3]. What came out from these studies is that the electroluminescence spectra of different materials (polyethylene, cross-linked polyethylene, polyethylene naphthalate) cannot be interpreted on the basis of the photo-physical properties of the polymer as investigated using UV-induced luminescence (photo-induced fluorescence and phosphorescence). The only way to reproduce the EL spectra is by irradiating the polymer with energetic electron beam. This suggests the processes associated with EL are degradative processes as well, which is obviously important in defining critical transport regime which marks the onset of electrical ageing. In this communication, we report for the first time the emission spectra associated with thin polypropylene films submitted to an electric field and an electron beam.

II. MATERIAL AND EXPERIMENTAL

A. Material and sample preparation

All the measurements were carried out on Bi-axially Oriented Polypropylene (BOPP) films of 17.8 μm thickness supplied by KOPAFILM, Germany. These are “hazy” films with rough surfaces to promote impregnation. The only additives contained in the BOPP film under study are pentaerythritoltetrakis(3,5-di-tert-butyl-4 hydroxyhydrocinnamate) and calcium stearate [4]. The former is known as Irganox 1010,

which is a sterically hindered phenol used as an antioxidant to abstract unstable radicals. Calcium stearate is a lubricant and an acid scavenger to neutralize any hydrochloric acid generated from reactions between the hindered phenol and residual chloride-containing catalyst. Irganox 1010 has a phenyl ring in its chemical structure as well as a carbonyl which is also present in the structure of calcium stearate. Light absorption in the near UV is therefore mainly due to the phenyl ring and carbonyl groups.

B. Electroluminescence a cathodoluminescence excitation

For electroluminescence measurements, both surfaces of the films were metallized with semi-transparent layers of gold deposited by cold sputtering (thickness: 30 nm, diameter: 50 mm). The films were sandwiched between two brass electrodes, one having a ring shape in order to allow light emission analysis under AC or DC field up to breakdown. Light emission analysis was performed at room temperature under high vacuum (about 5×10^{-7} mbar) in order to avoid partial discharges in the ambient atmosphere. Owing to the high dielectric strength of BOPP, DC electric field values up to 420 kV/mm (DC stress) and 250 kV/mm (sine AC crest field) were applied to the samples. Due to the low level of light detected under DC stress, electroluminescence spectra were realized under AC stress at different fields, spectra being recorded a short time after voltage application. For electron beam induced luminescence (also called cathodoluminescence -CL), the films were exposed directly to the beam without metallization. The electron gun, as described in [5], provides electrons of energy of up to 10 keV. 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. The sample surface is at about 40 mm from the exit of the electron gun, the axis of the electron gun being at an angle of 50° in respect to the normal of the sample for enabling light collection. Experiments were carried out at room temperature under a vacuum of 5.10^{-6} mbar. The electron current was about $0.5 \mu\text{A}$ in the experiments reported therein with a spot size of about 1 mm^2 . The beam current is independent from the energy of the electrons in the investigated energy range. Emission spectra have been recorded for different beam energies and for different times at the same beam energy.

C. Light detection set-up

Light detection is carried out by two systems: a cooled photomultiplier (PM) working in photon counting mode for integral light detection, and a grating monochromator (4.5 nm in resolution) coupled to a liquid nitrogen cooled charge coupled device (CCD) camera for spectral analysis which covers the wavelength range from 300 nm to 850 nm. The full set-up has been described elsewhere [2, 3].

III. RESULTS AND DISCUSSION

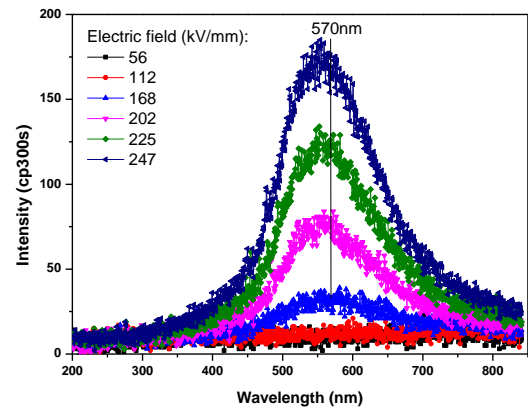
A. Electroluminescence and cathodoluminescence spectra

The electroluminescence spectra at different AC fields are shown in Fig. 1a. They have not been corrected for surface plasmon (SP) effects at the metallic electrodes that contribute to the EL at low electric field through a broad spectral

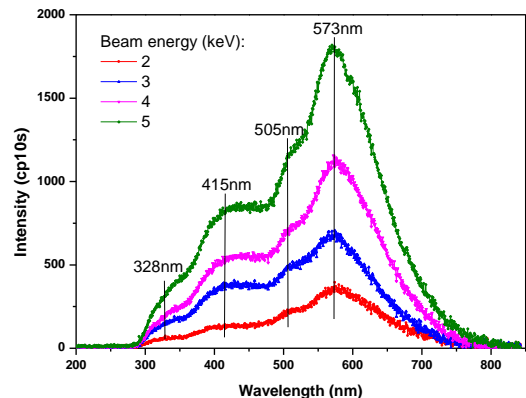
component peaking at about 800 nm. A full discussion of the SP effect can be found in [6]. From samples to samples, there is some variation of the SP contribution to the light intensity and the spectra shown in Fig. 1a correspond to a case where the SP has a weak contribution. Its contribution is therefore neglected in the analysis. The EL spectra peak at about 570 nm and appear broad and mainly structureless although a shoulder can be distinguished at about 500 nm. They roughly keep their shape for different fields.

The cathodoluminescence spectra are shown in Fig. 1b. They are much better resolved in wavelength due to the intensity of the emission ($\times 600$ for CL relatively to EL). The spectral shape does not change to a great extent vs. the beam energy with a maximum at 573 nm and three secondary shoulders at 505, 415 and 328 nm. However, the relative contributions at 328 nm and 415 nm increase with the field.

As observed in a variety of polymers, CL and EL spectra of PP films peak at the same wavelength and cover the same range suggesting they are organized along the same components. A tentative interpretation of the spectral components is given in the next section.



a. EL spectra of gold metallized BOPP films under 50 Hz AC at different fields. Spectra integrated for 5min at each field level.



b. CL spectra of BOPP films under electron beam at different energies. Spectra were integrated for 10s a short time after irradiation start.

Fig.1: Electroluminescence (a) and cathodoluminescence (b) spectra of BOPP films

B. Identification of the spectral components

As pointed out previously, the BOPP films under consideration contain some additives and their presence could play a role in the emission process. One straightforward experiment to check for a possible contribution of these additives to the emission is to record the UV-induced luminescence spectrum of the BOPP. Fig. 2a shows the UV-absorption spectrum of a film with an absorption maximum at 200 nm and two absorption shoulders at 230 nm and 280 nm. Absorptions at 200 nm and 230 nm are typical of $\pi\pi^*$ transitions in CC double bonds that are present in BOPP films through the phenyl ring of Irganox as well as unsaturations of the PP chain. The absorption at 280 nm is rather due to the $n\pi^*$ transition in carbonyl compounds [7]. Fig. 2b shows the fluorescence emission (transition from the first excited singlet down to the singlet ground state of the excited species) which is at maximum when excited at 230 nm and 280 nm (corresponding to the absorption maxima). Such kind of photo-induced emission is typical of PP fluorescence with a residual oxidation [7, 8]. Fig. 2c shows the phosphorescence peak excited at 250 nm (forbidden transition from the first excited triplet down to the singlet ground state of the excited species). It exhibits a maximum at 472 nm and two shoulders at 440 nm and 500 nm which have been associated with the presence of unsaturated carbonyls of the di-enone type [8]. Anyway in the context of our discussion, it appears that the EL and CL spectra are not organized around the same components as those revealed in photoluminescence, except may be for the shoulder at 328 nm visible in the CL spectra. A contribution of the natural fluorescence of PP cannot be ruled out.

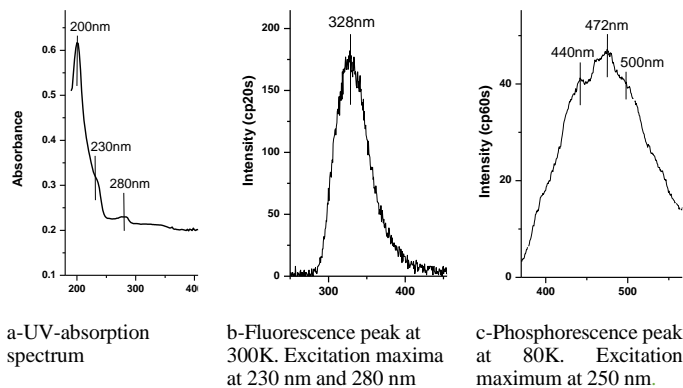


Fig.2: UV-absorption spectra (a), photo-induced fluorescence emission (b) and photo-induced phosphorescence emission (c) of BOPP films

Following the same approach, the shoulders at 415 nm and 505 nm in the CL spectra (and hardly distinguishable in the EL spectra even if the 505 nm component can contribute) have to be compared with the emission maxima of PP films in chemiluminescence and recombination-induced luminescence -RL experiments. The emission spectra of chemiluminescence in PP have been deeply investigated along the oxidation reaction [9]. It has been shown that at the beginning of the oxidation reaction, the emission has a quite narrow shape peaking at 415 nm and is due to the formation of carbonyl species (spectrum shown in Fig. 3b). In RL experiments where the light comes from charge recombination on the natural chromophores of PP the emission is broad and peaks at 505 nm as shown in Fig. 3c [8]. Following this picture, the EL and CL

spectra of PP could be interpreted as the superposition of four contributions: the fluorescence of the natural chromophore, a chemiluminescence component, the phosphorescence of enone compounds among the natural chromophore which act as recombination centers, and a fourth component at longer wavelengths tentatively attributed to excitation of by-products of the PP molecules.

C. Spectral reconstruction on the basis of elementary components

We have tried to reconstruct the emission spectra of CL and EL on the basis of the previous analysis. The spectra associated with fluorescence, chemiluminescence and recombination-induced luminescence are shown in Fig. 3. The shape of the fourth component associated with PP by-products is unknown. It has been deduced from fitting the CL spectra assuming each spectral component has a Gaussian shape with the same maxima as the known components. The fit to CL and EL spectra is shown in Fig. 4a and 4b respectively. Both spectra are nicely reproduced. The relative contribution of each elementary component is given in Table I. The different mechanisms do not contribute with the same weight in both processes: fluorescence and chemiluminescence have a stronger relative contribution to the CL spectrum.

D. Excitation mechanisms

In cathodoluminescence, the kinetic energy of electrons in the beam is the main source of excitation. They lose their energy through a diversity of channels among which impact excitation and impact ionization of the molecules. Impact excitation on the natural chromophores of PP will generate excitonic states that will further relax to their ground states (generating fluorescence and/or phosphorescence emission depending on the nature of the exciton) or react with the

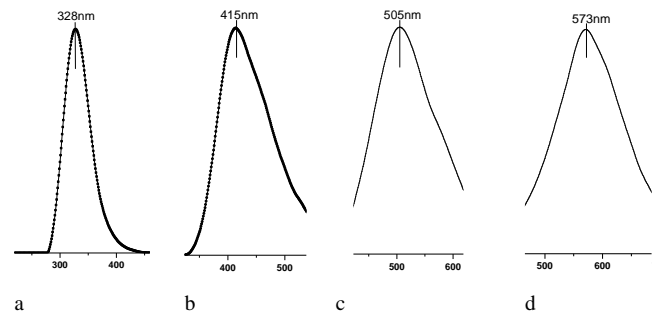
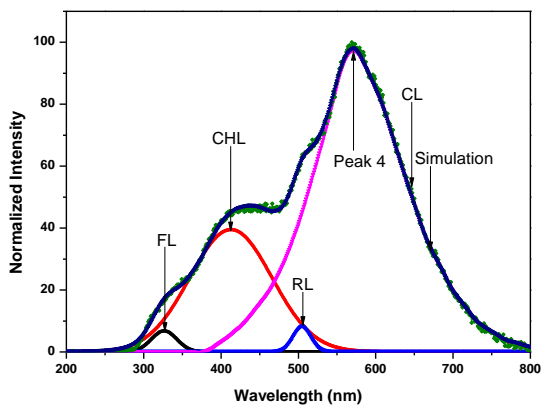


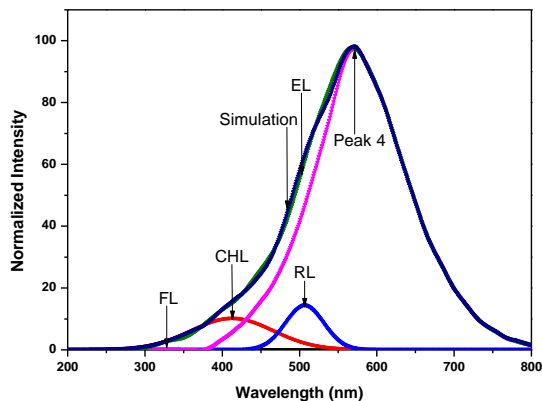
Fig.3: Spectral components associated with the fourth elementary processes. Fluorescence spectrum –taken from Fig. 2 (a), chemiluminescence spectrum –taken from ref. [9] (b), recombination-induced luminescence –taken from ref. [8] (c), unknown component – derived from fitting CL spectrum (d). Note that the spectra have been smoothed for eliminating noise.

TABLE I : RELATIVE CONTRIBUTION OF THE FOUR ELEMENTARY COMPONENTS IN CL AND EL SPECTRA

Component	328 nm	415 nm	505 nm	573 nm
CL	1.5%	25%	1.5%	72%
EL	0%	8%	5%	87%



a. Reconstruction of the CL spectrum



b. Reconstruction of the EL spectrum

Fig. 4: Reconstruction of the CL and EL spectra on the basis of four elementary components. FL stands for fluorescence, CHL for chemiluminescence, RL for recombination-induced luminescence and peak 4: unknown component associated to by-products generated in excited states

dissolved oxygen. It follows the possibility to emit light through the formation of carbonyl functions or polyene sequences (chemiluminescence). Impact ionization will be a source of positive charges and there is the possibility of charge recombination (generating light) when the incoming electron has already lost its kinetic energy, being trapped in the vicinity of the positive charge. Recombination can also occur between trapped electrons and trapped holes in diffusive recombination processes. In recombination processes, the emitting species will be those able to act as recombination centers i.e. those providing deep traps for electric charges. In PP, these centers are bound to CO species. Owing to the chemical degradation of the material under the electron beam, all these recombination processes can concern by-products leading to new components in the CL spectra. The CL experiment provides therefore the full set of excitation. In EL, the all set of processes can also be involved depending on the experimental conditions. We have shown that recombination between charges of opposite polarity provides the conditions for EL in polyolefins [6]. It has to be realized that recombination opens the way to chemiluminescence as well through the excitonic states created by the recombination process itself that can react with dissolved oxygen. Because a chemical pathway is open through reactive excited species, recombination can further affect newly formed chemical groups. In case of hot electron

processes and although the kinetic energies is not comparable in CL experiments (a few eV in EL vs. a few keV in CL), there is still the possibility for impact processes, with or without ionization. Impinging electrons with a kinetic energy of a few eV will not have the energy required for impact ionization (15 eV) but they can excite species that will relax through fluorescence and phosphorescence emission, or be stabilized to form transient ions (negative attachment – see [10]) able to subsequently dissociate into molecular fragments. Comparing CL and EL spectra, it appears that the components attributed to fluorescence of the natural chromophores and to chemiluminescence have a lower relative contribution in EL. However, EL spectra with different relative contributions of the elementary components have been recorded and this could be due to difference in the excitation conditions.

IV. CONCLUSION

We have compared the electroluminescence and cathodoluminescence spectra of thin polypropylene films. Like in other polymers, they are organized around the same components that we have tentatively assigned to specific molecular processes. It is striking their main components is due to byproducts of the polymer generated under an excited form. The results provide the evidence that electroluminescence is mainly related to molecular degradation and therefore to the ageing of the material under an electric field.

ACKNOWLEDGMENT

Thanks to Steve Boggs and Kopafilm Elektrofolien GmbH for supplying BOPP films. Thanks to the CSC for PhD grant.

REFERENCES

- [1] W. A. Hartman and H. L. Armstrong, "Electroluminescence in Organic Polymers", *J. Appl. Phys.*, Vol. 38, pp. 2393-2395, 1967.
- [2] D. Mary, M. Albertini and C. Laurent, "Understanding optical emissions from electrically stressed insulating polymers : electroluminescence in Poly(Ethylene Terephthalate) and Poly(Ethylene 2, 6-Naphthalate) films", *J. Phys. D: Appl. Phys.*, Vol. 30, pp. 171-184, 1997.
- [3] G. Teyssedre, L. Cissé, D. Mary, and C. Laurent, "Identification of the electroluminescence components of polyethylene", *IEEE Trans. Dielect. Electr. Insul.*, Vol. 6, pp. 11-19, 1999.
- [4] S. Boggs, private communication
- [5] G. Teyssedre and C. Laurent, "Evidence of hot electron-induced chemical degradation in electroluminescence spectra of insulating polymers" *Proc. ISEIM*, pp. 372-375, 2008
- [6] C. Laurent, G. Teyssedre, S. Le Roy and F. Baudoin, "Charge dynamics and its energetic features in polymeric materials", *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 20, pp. 357-381, 2013.
- [7] *Luminescence techniques in solid state polymer research*, Edited by Lev Zlatevitch, Copyright 1989 Marcel Dekker, INC.
- [8] -G. Teyssedre, L. Cissé, C. Laurent, F. Massines, and P. Tiemblo, "Spectral analysis of optical emission due to isothermal charge recombination in polyolefins", *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 5, pp. 527-535, 1998
- [9] P. Tiemblo, J. M. Gomez-Elvira, G. Teyssedre, F. Massines, and C. Laurent, "Chemiluminescence spectral evolution along the thermal oxidation of isotactic polypropylene", *Polym. Degrad. Stab.*, Vol. 65, pp. 113-121, 1999.
- [10] L. Sanche, "Dissociative attachment and surface reactions induced by low-energy electrons", *J. Vac. Sci. Technol. B*, Vol. 10 pp.193-200, 1992.