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# Contributing mechanisms to cathodoluminescence and AC electroluminescence spectra in polypropylene and polyethylene thin films

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**RESUME** – L'électroluminescence (EL) des isolants polymères est étudiée car elle peut permettre d'approcher les phénomènes de vieillissement électrique en fournissant la signature optique d'espèces excitées sous champ électrique. Dans ce travail, la nature des centres luminescents impliqués dans l'EL de deux types polyoléfines - polypropylène et polyéthylène, est étudiée, en comparant les spectres d'émission résolus en longueur d'onde à ceux obtenus sous excitation par faisceau d'électrons excitation (ou cathodo-luminescence – CL). La similarité des distributions spectrales du polypropylène montre que les mécanismes d'excitation de la luminescence sont les mêmes. Outre les similitudes remarquables entre spectres d'EL et de CL, indiquant une excitation de l'EL par un processus d'électrons chauds, nous montrons que les différents spectres peuvent être décomposés en une série de spectres élémentaires impliquant des groupes insaturés.

**MOTS-CLES** – Electroluminescence; Cathodoluminescence; Polypropylène; Polyéthylène; Vieillissement électrique; Mécanismes de luminescence.

**ABSTRACT** – Electroluminescence (EL) of insulating polymers is a subject of great interest because it is associated with electrical ageing and could provide the signature of excited species under electric field. In this work, the nature of luminescent centers involved in EL of two types of polyolefin thin films - Polypropylene and Polyethylene, is investigated, comparing wavelength-resolved emission spectra to those obtained under electron beam excitation named cathodoluminescence (CL). The common and unique spectral feature of Polypropylene and Polyethylene infers that they may mainly derive from the same luminescent mechanism. Aside the striking similarities between EL and CL spectra, pointing towards hot electron excitation in EL, we show that both spectra can be decomposed in a series of elementary spectra involving unsaturated groups.

**KEY WORDS** – Electroluminescence; Cathodoluminescence; Polypropylene; Polyethylene; Electrical ageing; luminescence mechanisms.

## 1. Introduction

Insulating polymers are used in a variety of applications in electrical engineering, such as cables, generators, transformers, capacitors, from personal computers to car manufacturing, from living facilities to military installations [1, 2]. Electrical ageing and breakdown in insulating polymers is of fundamental interest to the researchers, the design engineers, the manufacturers and the customers. In this respect, Partial Discharge (PD) is a harmful process leading to ageing and failure of insulating polymers. However, with the development of the materials and apparatus, PDs can be weakened or avoided in some situations, e.g. extra high voltage cables, capacitors, etc. Therefore, there is urgent demand for understanding electrical degradation mechanisms under high energy particles or electric field intensity, pushing the limit of electrical properties in insulating polymers.

Electroluminescence (EL) along with other luminescence techniques, like cathodoluminescence (CL) is an exciting field of research for probing insulating polymers, because it gives insight into electrical ageing and breakdown process, since firstly reported in 1967 by Hartman [3]. EL is an original technique, contributing to uncover the nature of charge transport mechanisms and electrical ageing. It provides a very interesting information, of photophysical nature, revealing excited states in the polymer, coupled to the electrical behavior of the material, especially with charge carriers in the material that are at the origin of the electroluminescence excitation through the exchange of kinetic or potential energy. However, the essence of EL and the links between EL and electrical ageing or breakdown are still debatable. Insulating polymers, such as polyolefins, have a large band gap (approximately 9 eV), with deep trapping centers mainly due to structural defects, impurities, or additives. EL can originate from hot electron carriers and/or recombination of charge carriers. More evidences and investigations need to be carried out to identify the excitation processes.

## 2. Materials and experimental

### 2.1 Materials

Measurements were carried out on different polyolefin materials, being bi-axially oriented polypropylene (BOPP) films of 17.8  $\mu\text{m}$  thickness supplied by KOPAFILM, Germany, cross-linked polyethylene (XLPE) films of 150  $\mu\text{m}$  thickness peeled from high voltage cable, and additive-free low density polyethylene (LDPE) of 120  $\mu\text{m}$  thickness investigated in a previous work [4]. BOPP films are “hazy” films with rough surfaces to promote impregnation of capacitors. These polyolefin materials are widely used in electrical and electronic industry. In an ideal structure, PP and PE should be non-luminescent materials in the visible domain since constituted of only saturated bonds. Luminescence arises because of the presence of in-chain defects such as oxidized groups or double-bonds, of impurities such as traces of catalysts, of additives (e.g. antioxidants) or of by-products (as crosslinking by-products in the case of XLPE). By comparing emission from these different polyolefins, it should be possible to unravel the different origins.

### 2.2 Light analysis setups

Both cathodoluminescence (CL, or called electron beam induced luminescence, EBIL) and electroluminescence (EL) analyses were performed at room temperature under high vacuum (about  $5 \times 10^{-7}$  mbar) in a specially-designed multipurpose chamber in order to avoid discharges in the ambient atmosphere. Light detection is carried out by 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. Both surfaces of samples were metallized with semi-transparent layers of gold as shown in Figure 1 (b) deposited by cold sputtering (thickness: 30 nm, diameter: 50 mm) for EL measurement. Otherwise, these samples don't need any pretreatment for the CL measurement.

Electron beam gun which employ focused electron beams as shown in Figure 1 (a) was used to provide electron beam of energy up to 5 keV for the cathodoluminescence measurement. The filament is at high voltage and the anode at the ground. The distance between the electron gun and the sample on the holder is about 40 mm. The axis of the gun is at  $50^\circ$  to the normal of the sample plane rendering possible light detection along the normal to the samples. The irradiation area is about 1  $\text{mm}^2$ . The beam current is about 1  $\mu\text{A}$ . Emission spectra were recorded for different electron beam energies from 2 keV to 5 keV and for different radiation time up to 210 seconds with the same beam energy.

The specially-designed electrodes – a ring electrode connecting to alternate current (AC) supply and a plane electrode connecting to the ground as shown in Figure 1 (b), provide uniform AC electric field for the electroluminescence measurement. The light emission from the center of the ring electrode through the center hole of the mask can be recorded by the CCD. The internal diameter of the ring electrode is 20 mm, the external diameter of that 30 mm. EL spectra were recorded under AC electric stress at 50 Hz frequency under field up to 250 kV/mm for BOPP and up to 45 kV/mm for LDPE.

Photoluminescence (PL) measurements can be also achieved in the same specially-designed multipurpose chamber at ambient atmosphere, excited with a xenon lamp which covers the wavelength range from 200 nm to 700 nm.

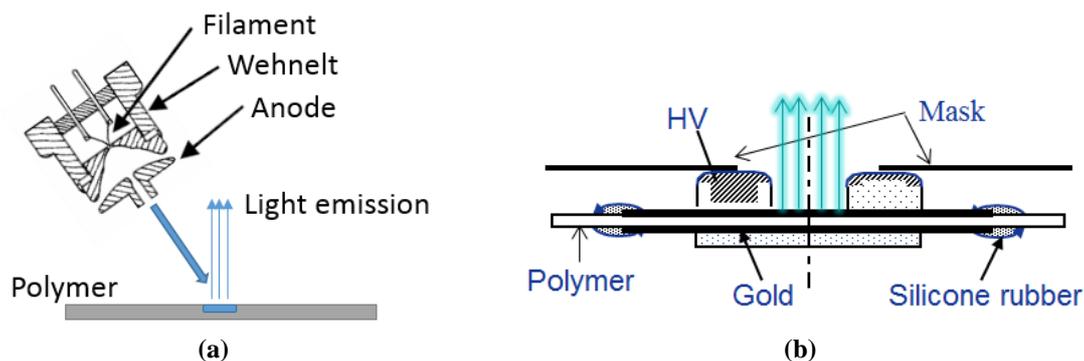


Figure 1 : Configuration of light analysis setups: (a) for CL and (b) for EL.

## 3. Results and discussions

### 3.1 AC EL spectral analysis

The EL spectra of Au-BOPP-Au samples are shown in Figure 2 (a). The emission spectrum can be analyzed as composed of two contributions with different field dependences: a contribution in the red domain of the spectrum, centered at 750-800 nm, dominating at low field, and another one centered at about 570-580 nm, dominating at relative high field. The red component emission has been attributed to relaxation of surface plasmons or to interface states [5]. It is dependent on the nature of the electrode metal. The bulk emission contains more information on physical and chemical process in the BOPP samples under high field. Figure 2 (b) shows the AC EL spectra of both PP from Figure 2 (a) and PE from previous work [4]. They have the same crest wavelength at about 570-580 nm and the same spectrum

shape except the red emission component, implying they derive from the same or similar luminescent mechanisms. It must be stressed that intensity of the red emission component changes somewhat from sample to sample. It is the dominant emission process at low AC field with gold-metalized samples [4].

The formation of excitons and subsequent relaxation through a dissociative pathway is one of the likely mechanisms for EL in PP and PE. Indeed, the fate of excitons formed upon recombination of electron/hole pairs has been investigated in polyethylene materials using density functional calculations and ab-initio molecular dynamics simulations. Two situations were investigated where excitons are self-trapped along a chain [6, 7] or trapped at chemical defects [7]. The relaxation can occur following different pathways depending on the case. When the excitons are trapped on a chemical defect, the relaxation pathway depends of the nature of the chemical defect leading to trapping of the charges, non-radiative recombination or homolytic bond-breaking. This is of course the last process that is relevant for damage. When the excitons are self-trapped along a chain, CH bonds breaking is promoted according to a recent calculation [8]. With the opening of a chemical route, by-products could be produced in excited states and be responsible for emission in a wavelength range that is not typical of the initial chemistry of the polymer. The electroluminescence features in PP and PE reveal their excitons transport and relaxation processes under electric field. PE and PP are both polyolefin, with similar CH bonds and by-products, maybe following the similar degradation route.

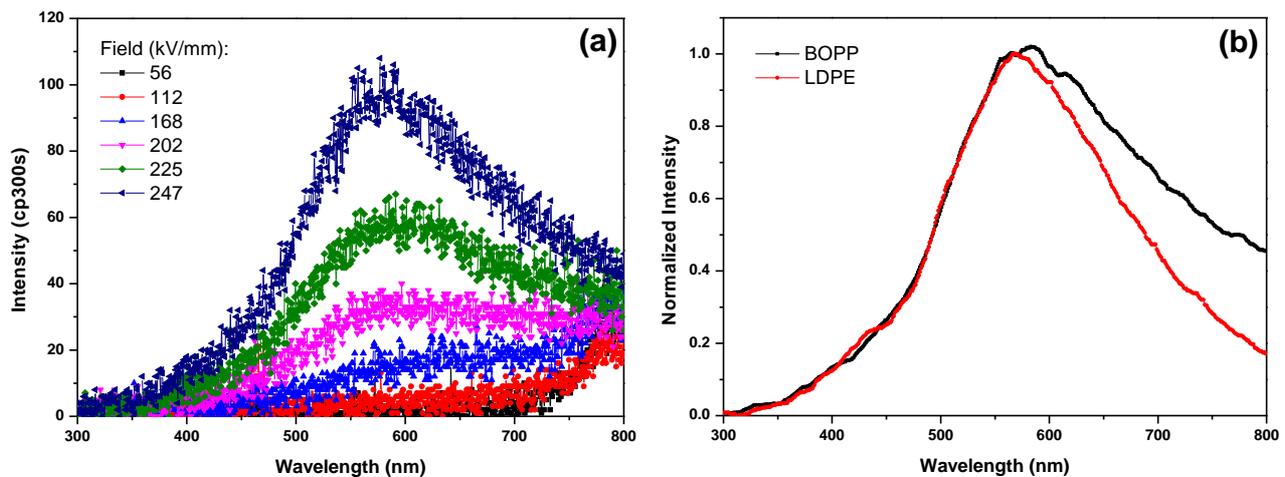


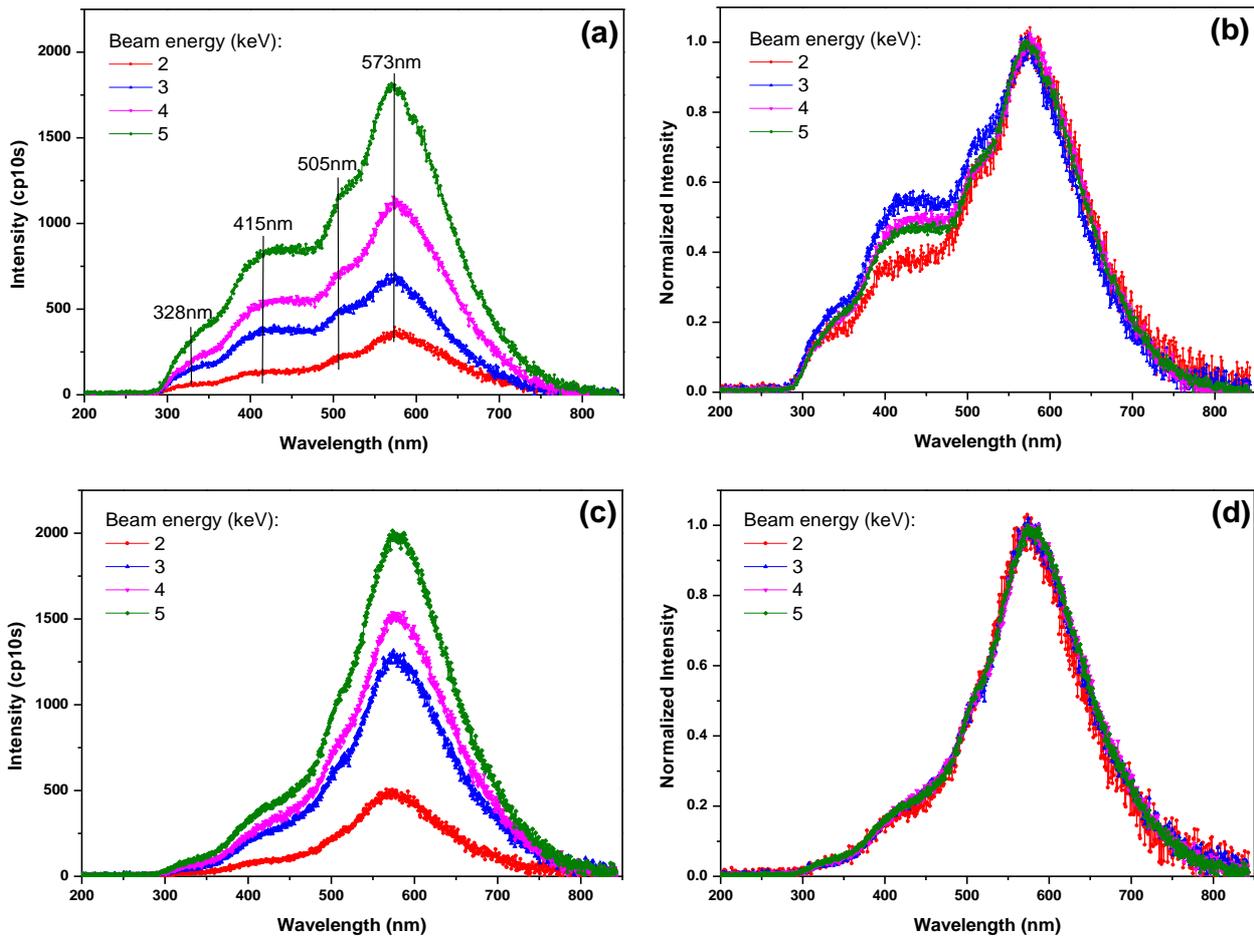
Figure 2 : EL spectra under 50 Hz AC stress, (a) Spectra of Gold metalized BOPP film integrated for 300 s at different fields; (b) Comparison of normalized EL spectra of BOPP under 247 kV/mm from Figure 2 (a) and of LDPE under 45 kV/mm from [4].

### 3.2 CL spectral analysis

In order to achieve more evidences of the common features in luminescence of PE and PP, we reproduced CL spectra of PP and PE films in Figure 3 for different e-beam energies. Figure 3 (a) and (b) are the CL spectra of BOPP, while Figure 3 (c) and (d) are the CL spectra of XLPE. They reveal a relatively strong emission (intensity is about x600 that of AC EL spectra) when comparing to AC EL in Figure 2. The CL emission is due to the energetic carriers injected in the samples during the electron beam radiation.

For PP samples, a main peak at about 573 nm and several shoulders at lower wavelength, i.e. 505 nm, 415 nm, and 328 nm are evidenced; for PE samples, the main peak is also at about 573nm but the shoulders components are weaker than in PP. The main peak in CL spectra also has the same wavelength vs. that in EL spectra, which infers that EL also derives mainly or partly from hot electron carriers. Both the BOPP films and XLPE films contain antioxidant and some other additives, but the nature is not the same in the two materials.

CL spectra exhibit high sensitivity to impurities, point defects, structural modifications, etc [9]. Exposure of materials to electron beam with such an energy induces a number of processes in the samples, which lead to the formation of secondary and backscattered electrons, and also generate characteristic radiation and bremsstrahlung, plasmons, and Auger electrons, which were studied in detail in [10, 11]. The electron beam can excite the deep traps to excited states or create electron-hole pairs at luminescent centers, which could then go back to ground level through transition, simultaneously emitting light. From normalized CL spectra of PP in Figure 3 (b), we can see that the shoulders have a dependence on the electron beam energy. These shoulders will be analyzed and decomposed below.



**Figure 3 :** CL spectra obtained with a CCD integration time of 10 s. (a), (c): Spectra of BOPP and XLPE films respectively, under different electron beam energies, (b), (d): Normalized CL spectra of BOPP film in (a), and of XLPE film in (c), respectively.

In order to uncover the nature of the CL main peak at 573 nm, we investigated the time-resolved spectral analysis of both BOPP and XLPE. CL spectra were carried out after different irradiation time with electron beam as shown in Figure 4 (a) and (c). The relative intensities of the four peaks or shoulders are not evidently variable as shown in Figure 4 (b) and (d), while CL intensity of both BOPP and XLPE decreases a lot within about 60 seconds and then decrease slowly with the radiation time as shown in Figure 5. The samples emit much less light after about 60 seconds. It can be speculated that at that time the samples have been almost aged. In our experiment, the irradiated area on both PE and PP samples have turned to be light brown from transparent, which directly proves that they have been aged during the electron beam irradiation. Along with the CL intensity decreasing with time, we can infer the CL emission is accompanied by electrical degradation of the insulating polymers. Furthermore, the CL spectrum - especially the main peak at 573 nm may be a signature of electrical degradation in these polymers.

### 3.3 Spectral analysis and reconstruction of elementary components

We have compared the normalized CL spectra of PE and PP in Figure 6 (a). Their spectra both contain the same main peak at 570-580 nm. However these shoulders in PE are weaker than those of PP. In order to investigate the origin of these peaks and shoulders, we have also compared CL and EL spectra of PP to Fluorescence (FL), Chemiluminescence (CHL), due to thermal oxidation [12], Recombination-induced Luminescence (RL) [13] of PP films as shown in Figure 6 (b). The FL in Figure 6 (b) can account for the component at 328 nm in CL. The photo-induced luminescence derives from a physical process and does not contribute to the electrical ageing. The UV-visible transmission spectrum of BOPP films reveal an absorption maximum at 200 nm, and two absorption shoulders at 230 nm and 280 nm, which are exactly the same two excitation peaks for the Fluorescence. The CHL has been investigated during the thermal oxidation [12]. It involves formation of carbonyl functions with a typical peak at 415 nm. The RL has been investigated by contacting the samples with a cold plasma powered at a frequency of about 5 kHz [13]. The light emission is due to the recombination of deposited charge carriers. This makes a little contribution to the CL shoulder at 505 nm, inferring that the charge recombination during electron beam irradiation is less. For the peak at about 570 nm, it has not been identified according to previous works. However, it has a direct correlation with electrical degradation according to our experiments forward. The CL and EL both have main peak at about 573 nm, inferring that they may derive from the same luminescence mechanism due to hot carriers effects and physical/chemical processes. However EL contains less

components at 328 nm and 415 nm, and more component at 505 nm, implying that recombination processes play a significant role under AC stress. The CHL component in the CL spectrum of PP is relatively strong, pointing to the formation of numerous of carbonyl functions and these chemical transformations make contributions to degradation. These elementary components together reflect electrical degradation in insulating polymers under electric stress.

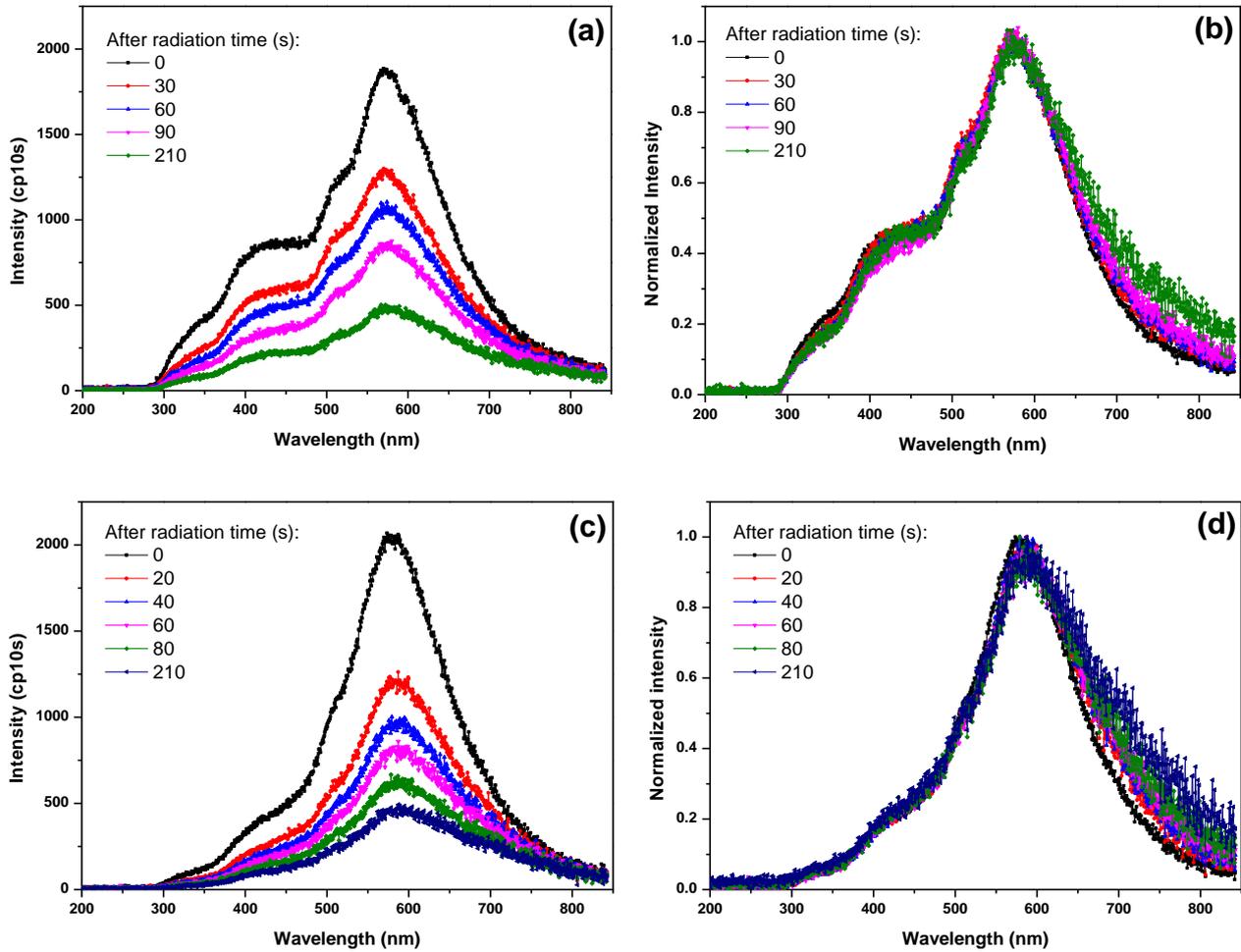


Figure 4 : CL spectra under electron beam energy of 5 keV after different irradiation time, (a) Rough spectra of BOPP film, (b) Normalized spectra of BOPP film from (a), (c) Rough spectra of XLPE film, (d) Normalized spectra of XLPE film from (c).

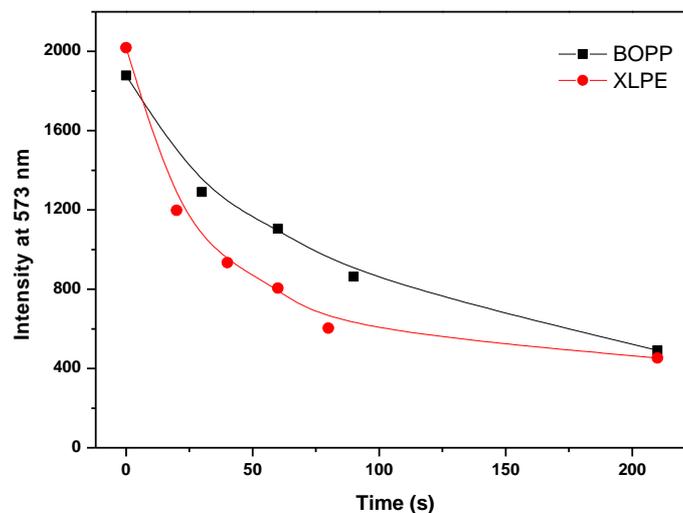


Figure 5 : CL intensity at 573 nm of BOPP and XLPE films as a function of irradiation time.

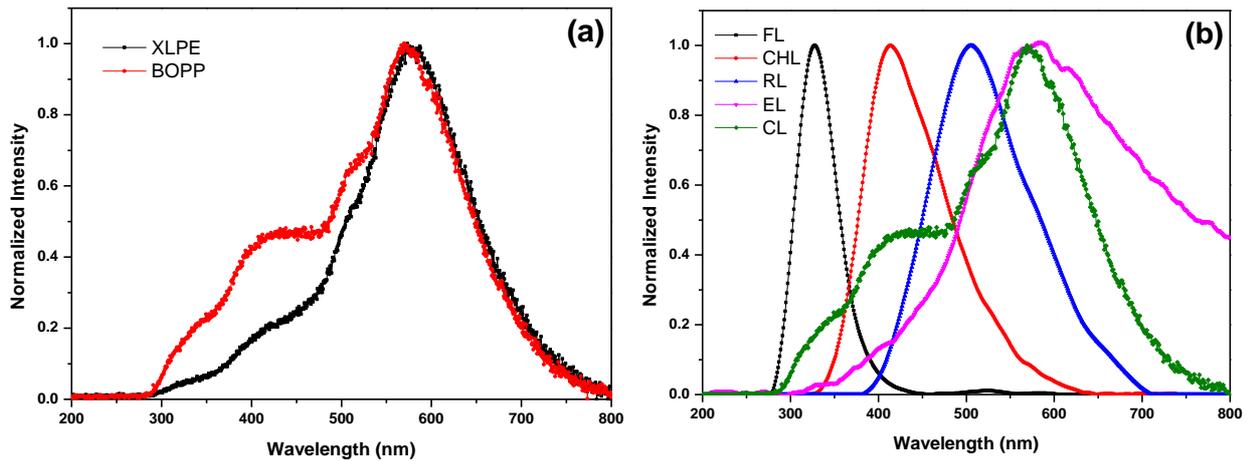


Figure 6 : (a) Normalized CL spectra of XLPE and BOPP films from Figure 3; (b) Normalized Fluorescence (FL, excited at 280 nm), Chemiluminescence (CHL), Recombination-induced Luminescence (RL), Electroluminescence (EL), and Cathodoluminescence (CL) spectra of BOPP, CHL taken from [12], RL taken from [13].

#### 4. Conclusion

Electroluminescence (EL) and Cathodoluminescence (CL) of polyethylene and polypropylene have been recorded and compared. We have shown that the CL of PP along with PE involves several bands already identified with other excitation sources and related to carbonyl and unsaturated groups. Emission spectra of PE and PP exhibit the same contributing processes, pointing towards chain defects and degradation products as luminescent species. The common and unique feature of EL and CL spectra is the appearing of a band at about 570 nm, inferring that they may mainly derive from the same luminescence mechanisms and physical/chemical processes. We also show that the spectra especially the band at about 570 nm have a direct correlation with electrical degradation of samples. Identification of these spectral components would be helpful to interpret the nature of light emission from polyolefin and other insulating polymers and to bridge the gap between space charge distribution and electrical ageing or breakdown.

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