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► To cite this version:

Bo Qiao, Gilbert Teyssedre, Christian Laurent, N. Shimizu. The significance of electroluminescence in polyolefins. IEEE International Conference on Dielectrics (ICD 2016), Jul 2016, Montpellier, France. pp.856-859, <10.1109/ICD.2016.7547751>. <hal-03943778>

HAL Id: hal-03943778

<https://hal.science/hal-03943778v1>

Submitted on 19 Jan 2023

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The significance of electroluminescence in polyolefins

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Abstract— Electroluminescence has been widely reported in large band gap insulating polymers under any kind of electrical stress, being ac, dc, impulse etc. but its significance is still the matter of debate. It was first investigated in the late seventies in divergent field experiments (i.e. using needle electrodes embedded in the material) as a precursor of electrical treeing. Later on in the nineties, uniform field experiments (i.e. using semi-transparent or transparent electrodes on top of a polymer film) were carried out. The main advantage of the divergent field configuration is the possibility to focus physical/chemical microanalysis in the tiny high field region around the needle tip for characterizing material degradation, which is not easy under uniform field owing to the low level of deterioration and its likely local character. The main advantage of the uniform field configuration is the possibility to correlate electroluminescence with real-time space charge distribution measurements as well as to acquire wavelength-resolved emission spectra. In this communication, we discuss the consistency of the experimental results obtained in divergent/uniform field experiments and the cross-fertilization between the two as regards the relationship between electroluminescence and material degradation.

Keywords—*Insulating polymers; electroluminescence; polyethylene; divergent field; uniform field; electrical ageing.*

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 other factors depending on the working environment (e.g. irradiation, humidity, etc.). Their use in practical applications is limited by their lifetime under a given stress, and not that much by their intrinsic properties [1]. 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, there are practical situations where the existence of PD must absolutely be 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 and in the driving factors in their intrinsic limits. One of the key challenges in investigating the electronic properties of this class of 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 [2]. Detecting the optical emission from the investigated material under electric field (electroluminescence - EL) provides a way to couple transport processes and dissipative processes as a possible signature of deleterious reactions at the atomic level [3].

Electroluminescence of insulating polymers has been reported for a variety of materials for many years starting in 1967 [4] where the first consistent experiments were performed on films of polyethylene, polyethylene terephthalate, etc. The experiments were carried out under vacuum for avoiding gaseous discharges in the atmosphere. The samples were pressed between two electrodes, one of them being a transparent and conductive glass. The emission spectrum was realized for polyethylene films using optical filters. In their conclusion, the authors propose that electrons injected from the electrodes or generated from bound states into the material are accelerated by the field and collide with some luminescent centers. Owing to the similarity with the luminescence excited by UV and by shorter radiation, they concluded that carbonyl groups should be at the origin of the emission itself. In spite of the novelty of their observation and interpretation, there was no report on EL under uniform field in the next few years. The topic was reactivated in the late 70ths when different groups started to work on the initiation phase of electrical treeing trying to understand the formation of trees in the absence of partial discharges [5]. Divergent field experiments dominate until the early 80ths when uniform field was reinvestigated for correlating EL and space charge. Since then, each type of experiment brought a piece of the puzzle with the physical-chemical analysis of the material deterioration in the luminescent volume around a needle electrode, and a clear correlation between electroluminescence occurrence, the existence of space charge and some specific regime of charge transport for uniform field experiments.

In this paper, we present a short summary of electroluminescence experiments carried out in divergent and in uniform fields and give the main conclusions drawn in each

case. In a second part, we introduce spectral analysis as a step forward in the understanding of electroluminescence. In a third part, we cross-correlate the results, show their consistency and propose an interpretation of the processes at play in both cases, leading to a unique picture of the physicochemical mechanisms involved in polyethylene under electrical stress.

II. ELECTROLUMINESCENCE FEATURES

A. Divergent field

A review of the topic has been published in [6, 7] where the references cover the period up to the 1998, i.e. a time window where most of the divergent field experiments were developed. We just summarize below the salient features of the results:

- the emission comes from a tiny region around the needle electrode (which size is of the order of magnitude of the curvature radius at needle tip) and can be detected under ac, impulse and other time varying voltage waveforms (including grounding the electrode after dc charging). EL has never been reported under constant dc stress in divergent field. This was explained in terms of excitation conditions: EL needs either hot electrons production or bipolar recombination, or both processes acting together. Time varying stress provides conditions for both whereas dc stress under a divergent field leads to the formation of a stable space charge cloud around the needle which screens the field at the tip preventing further injection.

- EL is detected at any temperature but is more easily analyzed at low temperature (e.g. liquid nitrogen temperature): this is due partly to the increase of breakdown strength with a decreasing temperature allowing a higher stress to be applied without tree initiation, and partly to the quenching of excited states by the dissolved oxygen, a process which is inhibited at low temperature.

- EL is sensitive to the nature of the gas dissolved in the amorphous parts of polyethylene. Notably, degassing the sample before testing leads to a substantial increase of the time-to-tree initiation under a given stress. This has been explained by the reduction of the degradation rate of the material when the concentration of oxygen is lowered. Oxygen molecules in the polymer under stress act as a catalyst for the degradation.

- long term application of the stress (before electrical tree initiation) leads to the formation of a spherical region at the needle tip with different optical properties than the rest of the material. Microanalysis of the material properties in this region called for physical chemical deterioration characterized by: (i) an increase of C=C and C=O bonds (using FTIR); (ii) the apparition of free radicals (using ESR); (iii) the formation of small voids ($< 0.5 \mu\text{m}$) (using SEM); (iv) damage to the structure of the lamellae (using TEM). This clearly indicates a degradation of the material in the region of higher stress. This domain has been called "deteriorated region".

- the diameter of the EL emitting zone and the diameter of the deteriorated region increase with the increase of the stress (see Fig. 1). Moreover, emitting region and

deteriorated region have the same diameter for a given stress. This allows to associate degradation and EL in a framework where both processes occur in the same volume. This does not demonstrate that EL is the source or a consequence of the degradation but that both phenomena are linked.

- the question of a threshold for EL onset has been discussed at length in the literature because it was believed it could be used as a material intrinsic characteristic in that above this field, rapid degradation takes place from hot electrons and carrier recombination. Within the Field Limiting Space Charge theory [8], the EL threshold corresponds to a critical field above which injected charges become highly mobile at needle tip leading to the expansion of a space charge cloud which density increases as the square of the applied voltage. This has been checked in different materials [8, 9] and preliminary measurements presented in [10] tend to show the EL onset is the critical field. However, measurements on polyethylene contrast with this view and the existence of a steep increase in carrier mobility has not been proven. EL is explained in terms of recombination between charges alternatively injected in positive and negative half cycles of the ac voltage. In that case, a physical threshold can be defined if the measurement is not limited by the sensitivity of the set-up (experimental limitation) because the process of charge injection is highly non-linear. Space charge could be injection limited as opposed to the FLSC model where it is mobility limited.

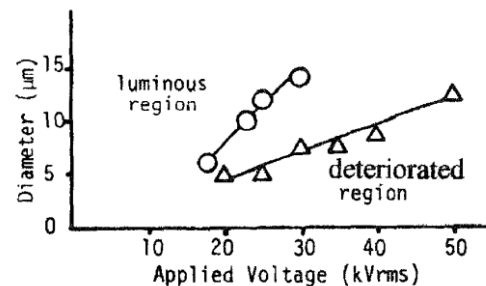


Fig. 1. Diameter of luminescence region and deteriorated region as a function of applied voltage. From [7].

B. Uniform field

A review of the topic has been published recently [11] where the references cover the period up to the year 2012, i.e. a time window where most of the uniform field experiments were developed. We just summarize below the salient features of the results:

- EL is detected at any temperature and under any kind of stress. Contrary to the case of a divergent field, the uniform field provides conditions for charge injection at both electrodes. Bipolar recombination can therefore occur after the injected charges have transited through the thickness of the sample (being usually $20 \mu\text{m}$ to several $100 \mu\text{m}$ thick in lab's experiments).

- Combined EL and real-time spatially-resolved space charge measurements under dc field show that bipolar charge recombination is the main driving factor in EL excitation under dc stress. Numerical models incorporating bipolar charge injection, transport, trapping and recombination have been developed that reproduced nicely the main features of EL.

Location of the domains where the recombination rate is the highest changes as a function of the stress (which controls charge density and their location).

-Combined EL and real-time spatially-resolved space charge measurements under 50 Hz ac field demonstrate that the conditions for EL excitation exist in the vicinity of the injecting electrodes. Numerical modelling based on the same physical processes as under dc shows that a much higher density of states has to be introduced at the interface electrode/polymer when compared to the bulk density of states. ac stress provides the conditions for charge recombination in a thin region (a few microns thick) in contact with the electrodes.

-The question of a threshold for EL emission has also been discussed in the situation of a uniform field. Under ac stress, the same conclusion is drawn as in the case of a divergent field: EL seems injection limited rather than mobility limited and a threshold can be defined at the onset of non-linearity in the charge/field characteristic. Under dc stress and in the absence of any internal space charge prior to the application of the stress, a threshold in time can be defined at a given stress, being the transit time of injected carriers that need to interact for recombination to occur [3]. Once the time under stress is greater than the carrier transit time, there is a non-zero probability for bipolar charge recombination and therefore no threshold for EL emission. However, the recombination rate is highly non-linear in field and a threshold can be defined at the onset of the non-linearity.

III. SPECTRAL ANALYSIS

A. Divergent field

Interference optical filters (typically 50 nm width) covering the entire visible range (300 nm to 800 nm) were most often used in the light path of a photomultiplier (PM) in order to get a rough evaluation of the emission spectrum of polyethylene. Wavelength-resolved spectral analysis was seldom used because of the faint emission, but some data were collected at liquid nitrogen and room temperature. These data have been replotted in Figure 2. It can be seen that the spectra obtained by different groups are consistent with an emission maximum between 500 nm and 600 nm, and a low contribution at lower wavelengths.

B. Uniform field

Wavelength-resolved emission spectra from polyethylene films under a uniform field have been investigated thoroughly by coupling a low dispersion grating to very sensitive detectors based on CCD (charge-coupled device) technology [16]. An example of such spectra acquired under ac stress is shown in Figure 3. They exhibit similar structures as the spectra obtained under divergent field with a maximum of emission at 573 nm and a small contribution at lower wavelengths. A contribution is seen in the domain 700 nm-800 nm and this was ascribed to radiative surface plasmons excited at the surface of the metallic electrodes, a process well documented in Metal-Insulator-Metal tunnel junctions and first reported in Metal-Polymer-Metal sandwich in 1999 [17].

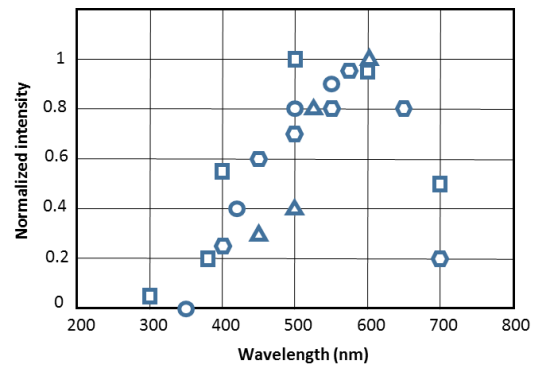


Fig. 2. Emission spectra from LDPE samples tested under a divergent field configuration and ac stress, from different groups: square from [12], triangle from [13], circle from [14], and diamond from [15]. All the spectra were obtained using interference filters, except the data by Pietsch [14] which were acquired with a spectrometer.

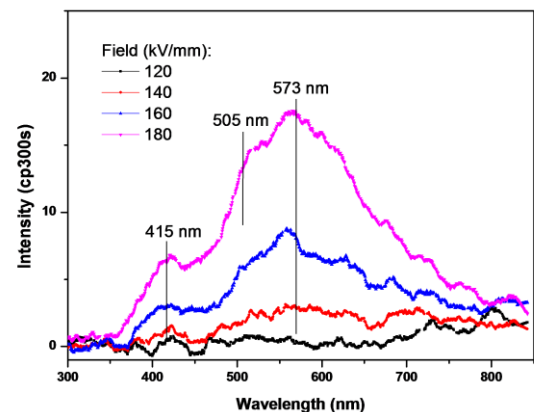


Fig. 3. Emission spectra from LDPE film at different fields (uniform field, 50 Hz ac). From [16].

C. Interpretation of the electroluminescence spectra

Electroluminescence spectra have been recently interpreted in polyethylene and polypropylene with the help of a panoply of luminescence spectroscopies (including photo-, chemi-, cathodo- and recombination-induced luminescence) [16]. They can be reconstructed from three elementary components being (i) chemiluminescence emitted during carbonyl functions formation with a typical signature at 415 nm, (ii) recombination-induced luminescence on deep traps acting as recombination centers (natural chromophores of the polymer) with a typical signature at 505 nm and (iii) a component peaking at 573 nm and tentatively assigned to by-products of field-induced reactions. This is shown in Figure 4 where the spectrum of Figure 3, once corrected from the contribution of surface plasmons, is reconstructed on the basis of the elementary components –see [16]. Surprisingly, there is no contribution of fluorescence of the polymer chromophores contrary to the case of cathodoluminescence spectra. This has been explained by a quenching of the singlet exciton (weakly bounded) by the electric field.

IV. THE OVERALL PICTURE

EL spectra from polyethylene are similar under divergent and uniform fields indicating the processes at play in both

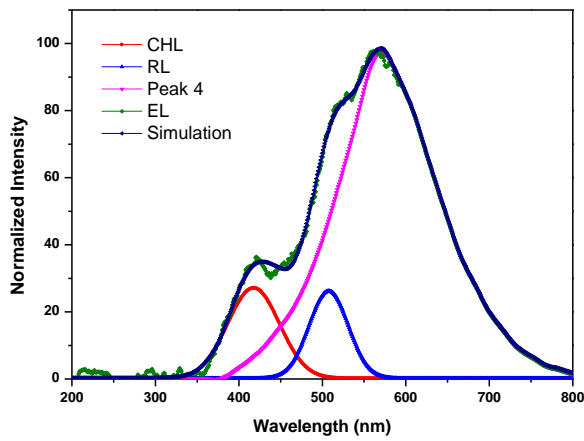


Fig. 4. Reconstruction of the electroluminescence spectrum of polyethylene on the basis of three elementary components, as explained in Table I. Taken from [16]. CHL stands for chemiluminescence; RL stands for recombination-induced luminescence; EL stands for electroluminescence; Peak 4 is associated with field-induced by-products of PE.

TABLE I. CONTRIBUTION OF EACH ELEMENTARY COMPONENT IN LDPE EL SPECTRUM RECONSTRUCTION

Chemiluminescence in its early stage Peak max at 415 nm	Recombination-induced luminescence Peak max at 505 nm	Polymer by- products Peak max at 573 nm
11.5%	8.5%	80%

situations are the same. Emission spectra are reconstructed using three elementary components. One of those is chemiluminescence ($C=O^* \rightarrow C=O$) which indicates that field-induced oxidation is taking place. This is consistent with a degradation scheme already proposed for polyethylene where radicals generated under stress react with oxygen initiating an auto-oxidation process [7]. It follows the formation of excited species, radicals, hydroperoxide and $C=O$ bonds. The scheme is supported by the physical chemical analysis of the deteriorated region. One other component of the EL spectrum is due to charge recombination on the natural chromophores of the polymer (conjugated $C=C$ and $C=O$ unsaturations of the polymer chain). Bipolar recombination has been advocated as the source of electroluminescence under divergent and uniform fields. This gives a totally consistent picture of the physical processes at play. Finally, the third component of the EL spectrum has been ascribed to some radiative reaction involving by-products. With the opening of a chemical route, by-products could be produced in the excited state and be responsible for emission in a wavelength range that is not typical of the initial chemistry of the polymer. The main peak in electroluminescence could reveal such degradation process.

A still open question is the localized or delocalized character of the degradation under uniform field. Under dc stress, the recombination domains –where degradation is occurring, is within the bulk. Under ac stress, the EL is occurring at the interfaces electrode/polymer where the electronic properties control the build-up of local currents which are possible sources of local degradation.

V. CONCLUSION

The significance of electroluminescence from insulating polymers has been discussed since a long time, especially in polyethylene-based materials. Excitation mechanisms and the relationship to electrical degradation were the most tackled questions. We demonstrated that divergent and uniform field experiments carried out on polyethylene provide consistent and complementary results leading to a global picture. EL tells us that chemical reactions induced by the field are ongoing and as such constitutes a warning for the material withstanding. It also opens several routes for investigating physical chemical processes associated with charge injection and space charge.

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