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# SPACE CHARGE INDUCED LUMINESCENCE IN EPOXY RESIN

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*Dielectric breakdown of epoxies is preceded by a light emission from the solid state material, so-called electroluminescence. Very little is known however on the luminescence properties of epoxy. The aim of this paper is to derive information that can be used as a basis to understand the nature of the excited states and their involvement in electrical degradation processes.*

## Introduction

In spite of their use in components for power generation, transmission and distribution, the degradation mechanisms of epoxies under field are not well-known. They have been primarily studied under divergent field situation where the generation and development of electrical treeing was evidenced after the formation of a void in the material [1, 2]. Little is known of the physical processes that lead to void formation. However, light emission has been reported to occur before void formation under long term stress [3], or before breakdown under short term stress [4]. This field-stimulated emission, called electroluminescence (EL), has been reported in other insulating polymers. Contrary to what is observed in semi-conducting organic materials [5] the emission spectrum of the EL is not identical to the photoluminescence spectrum, underlining that specific excited states are promoted during field application [6]. Analyses performed on polyolefins and polyesters have shown that the EL lies in a wavelength range typical of radiative relaxation occurring from the lowest excited triplet states available in the solid. Being triplet, these states have a long life time (ms to s) and are therefore chemically reactive. They can open a pathway for chemical reactions that could be linked to electrical ageing and dielectric breakdown.

The present work is carried out on epoxy resin samples prepared from an Araldite base (CY1301) mixed with an hardener containing amine groups (HY1300). Two sources of excitation were used in addition to the electric field to help the interpretation. In photoluminescence (PL) experiment, the light is stimulated by the absorption of photon whereas in recombination-induced luminescence (RIL), the light is due to the radiative recombination of charges of opposite sign that have been brought to the sample surface. On the basis of the information gathered by using these two techniques, it is thought that the origin and significance of the EL can be approached.

## Experimental

Whatever is the excitation source, luminescence detection was realized by using a photomultiplier working in photon counting mode and a monochromator coupled to a liquid nitrogen cooled CCD camera.

The source of photon is a Xenon lamp of 150 W that produces a continuous spectrum in the range 200-1000 nm. The lamp is coupled to a double-pass irradiation monochromator (Jobin-Yvon type H10UV with a spectral range of 250-750 nm) used to select the excitation wavelength with a bandwidth of 2 nm. An image of the irradiation slit is focussed onto the sample surface through a quartz lens. A mechanical shutter is used to cut off the irradiation beam which allows us to record several consecutive spectra during the phosphorescence decay of the material.

The technique that we used to analyze recombination induced luminescence has already been described elsewhere [7]. Charges of both polarities are deposited on films upon contact with a silent discharge produced in helium at atmospheric pressure between two parallel electrodes. The decay of light emitted by the sample after discharge switch off is analyzed in both the integral and wavelength-resolved forms. At short time, luminescence excited through processes other than radiative recombination was recorded. The analysis of the decay kinetics of integral light allowed us to unambiguously determine the time range where recombination was the dominant excitation mechanism. The related emission spectrum was identified accordingly.

The preparation steps of the sample for electroluminescence experiments have been described elsewhere [8]. Films were gold coated by cold sputtering and a ring of silicon rubber was deposited to prevent stray light detection due to uncontrolled field at the periphery of the metallized area. The sample is positioned between two cylindrical polished electrodes. The bottom electrode is connected to the earth. The top electrode is a ring which allows the light collection. Measurements were performed at room temperature under a pressure of $10^{-6}$ torr using an AC voltage excitation.

## Results and discussion

**The typical photoluminescence spectrum** recorded at liquid nitrogen temperature (LNT) during the excitation is shown in ***fig. 1***. The emission peak at ~410 nm is the fluorescence emission that is also detected at room temperature (RT) whereas the broad emission peaked at higher wavelength is interpreted as a phosphorescence component. The difference between spectra obtained at LNT and RT gives a rough estimation of the phosphorescence spectrum shape. This has been done as shown in Figure 1, and leads to a phosphorescence emission peaked at about 500 nm. Further confirmation of the phosphorescent nature of the emission is obtained by a kinetic analysis of the spectral shape carried out after switch-off of the excitation beam. As shown in ***fig. 2***, the emission spectrum can be resolved in time during the natural decay of the phosphorescence (i.e. different spectra were recorded in a row just after excitation beam switch-off) whereas there is no trace of the fluorescence in agreement with its fast decay (order of $10^{-8}$ s).

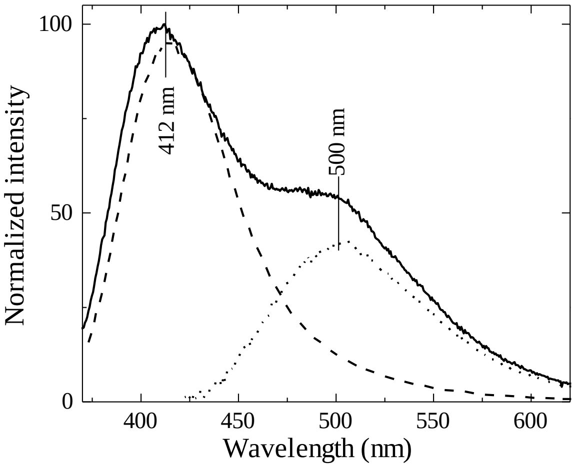

***Fig. 1*** *RT (dashed) and LNT (solid) photoluminescence emission spectra for the cured resin ($\lambda_{exc}$=350nm). The difference (dotted line) represents phosphorescence.*

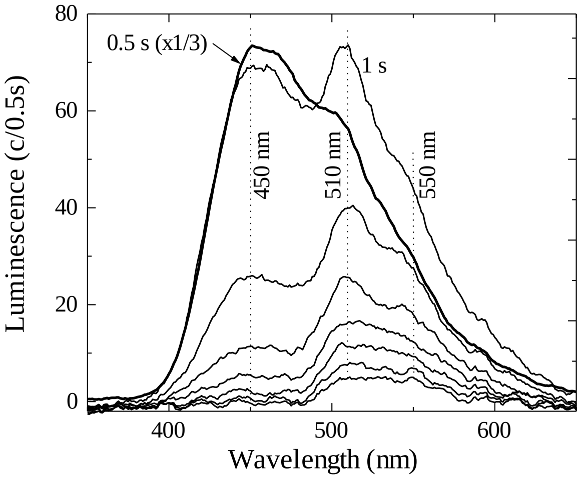

***Fig. 2*** *Phosphorescence decay of cured resin. Spectra recorded every 0.5 s, excitation wavelength at 320 nm.*

Three components have been detected at 450, 510 and 550 nm. The decay lifetimes estimated for these three components are 0.45, 1.2 and 1.4s, respectively. It is clearly seen that at least two and possibly three different chromophores are contributing to the phosphorescence emission owing to the different kinetics seen in the spectral shape. This is further confirmed by the strong variation in phosphorescence spectrum versus excting wavelength, ***fig.3***.

The assignment of the photoluminescence components to given chemicals is not straightforward. A first question is to know if the fluorescent specie could also be at the origin of one component of the phosphorescence. This can be checked by analyzing the excitation spectra recorded at 450 nm and 510 nm. Although there is a difficulty in separating these two components because of overlap of their phosphorescence spectra, the excitation of the 450 nm peak is effective in the range of excitation of the fluorescence whereas the 510 nm peak is excited at about 400 nm. It seems therefore that the fluorescence at 410 nm and the phosphorescence at 450 nm could have the same origin, whereas the 510 nm could be due to a phosphorescent specie that does not give a fluorescence emission. The phosphorescence of Bisphenol A epoxy resin has been reported in [9] with an emission at 460 nm and two excitation peaks at 275 nm and 350 nm. It is clear that this component of the phosphorescence corresponds to the 450/460 nm component detected in our study. It has been attributed to the formation of a triplet excimer of unspecified nature [9]. The results obtained here allow to associate fluorescence (410 nm) and phosphorescence (450/460 nm) to the singlet and triplet excimer of a chromophore that is part of the polymer chain and that was already present in the liquid resin before its polymerization.

**A typical recombination-induced luminescence spectrum** is shown in ***fig. 3***. It is clear that it is organized around the same components as the photo-induced phosphorescence emission of the resin, although their relative contribution is slightly different. Two peaks are clearly detected at about 470 and 540 nm. A shoulder is also seen at about 500 nm. This leads to the conclusion that the chromophores responsible for the phosphorescence emission play also the role of recombination centres.

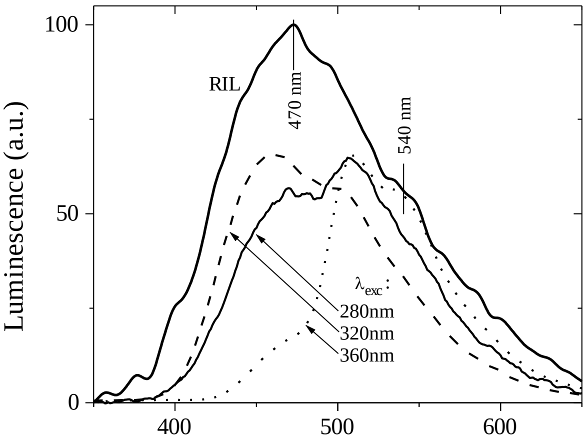

***Fig. 3*** *Emission spectrum due to charge recombination (RIL) compared to photo-induced phosphorescence excited at different wavelengths.*

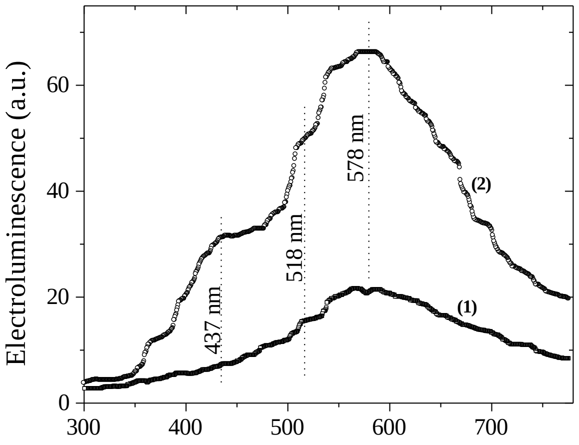

***Fig. 4*** *Electroluminescence spectra, 298 K, ac voltage excitation source at (1): 20 kV/mm; (2):35 kV/mm.*

**Two different electroluminescence spectra** were recorded at different levels of field, 21 kV/mm and 35.7 kV/mm, using an integration time of 10 min. They are shown in ***fig. 4***. The spectra recorded at 21 kV/mm gives one peak at 578 nm whereas the spectra recorded at 35.7 kV/mm shows the same peak and two additional shoulders at 518 and 437 nm (see figure 4). When comparing the spectrum due to charge recombination, common structures appear at 435 nm and 518 nm. These components could therefore be due to the recombination of charges that is likely a process occurring also in electroluminescence. Charge-recombination is expected to occur in electroluminescence if the excitation involves impact-ionisation by hot carriers or bi-polar injection. In both cases, thermalized carriers are generated, after the ionisation event or the injection, respectively. As a consequence, there is a region where carriers of opposite signs are being trapped. These carriers are likely to recombine, giving rise to the component of the luminescence that has been isolated in charge recombination-induced luminescence experiments.

However, the peak at 595 nm has never been observed using other kinds of luminescence excitation. It is clearly located in the wavelength domain of phosphorescence and might be another phosphorescent component likely associated with the degradation of the material. Electroluminescence would therefore involve relaxation of excited states through irreversible pathway, which would link the emission and the deterioration of the resin. Further investigations are needed to give definitive evidence of this finding.

## Conclusion

The luminescence properties of bisphenol A type epoxy resin have been investigated to land a support to the interpretation of the electroluminescence which is thought to be linked with electrical ageing and breakdown mechanism. Photo- and recombination-induced luminescence have been used to derive the emission characteristics of chromophores and recombination centres. Although the picture is far from being complete, we have shown that the recombination centres in the cured resin are part ot the chain of the base resin itself. The emission spectrum recorded during charge recombination is in the phosphorescence region as currently observed in insulating polymers. The emission spectrum of electroluminescence is also located in the phosphorescence region, but its form cannot be accounted for only by the recombination spectrum. The other component of the EL emission could be related with molecular degradation of the resin. Although further investigation is needed to understand more completely the luminescence properties of the resin in relation with the ageing process, this work lands a support to the comprehension of EL in this material.

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