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Photoluminescence, Recombination Induced Luminescence and Electroluminescence in Epoxy Resin

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ABSTRACT

Dielectric breakdown of epoxies is preceded by light emission, or so-called electroluminescence, from the solid-state material. Very little is known about the luminescence properties of epoxies. 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. Three different kinds of stimulation were used to excite the material luminescence. Photoluminescence was performed on the base resin, the hardener and the cured resin. Luminescence excited by a silent discharge has been analysed to identify which of the luminescent centres are optically active upon the recombination of electrical charges and could therefore act as charge traps. Finally, the electroluminescence spectrum has been acquired and compared with the previous ones. Although the identification of the origin of these emissions is far from being complete, it has been found that the photoluminescence from the cured resin is due to in-chain chromophores, which acts as trapping centres. The excited states involved in photoluminescence also seems to be involved in electroluminescence, but other components are detected as well, which could be due to the degradation of the resin molecule under the effect of the electric stress.

1. 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 on 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, emphasising that specific excited states are promoted during field application [6]. Analyses performed on polyolefins and polyesters have showed 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 lifetime (order of 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 available information on luminescence properties of epoxies is scarce. The objective of this paper is to provide an insight into these properties to form a basis for the interpretation of the electroluminescence spectrum.

The present work is carried out on epoxy resin films. Two sources of excitation were used in addition to the electric field to help the interpretation. Photoluminescence (PL) was used, in which the light was stimulated by the absorption of photon. Recombination-induced luminescence (RIL) was also used; the light in this case was due to the radiative recombination of charges of opposite sign that have been deposited on the sample surfaces. A short description of these techniques is given in the experimental section.

Photoluminescence (PL) experiments allows one to investigate the reversible de-excitation pathway by which the excited states of a species return to the ground state of the same chemical (also called “physical pathway” as opposed to “chemical pathway” [7]). The electronic transitions involved in photoluminescence can be decomposed into fluorescence and phosphorescence components for a transition from the first excited singlet and triplet state to the ground state respectively. The fluorescence emission is usually dominant at room

temperature (RT). It is convenient to work at liquid nitrogen temperature (LNT) in order to observe the phosphorescence emission. Fluorescence and phosphorescence have very different lifetimes; this allows a differentiation of the two processes on the basis of dynamic measurements. The phosphorescence decay spectrum can be recorded whereas the fluorescence vanishes too quickly (life time of the order of 10^{-8} s) to be detected by using conventional detection techniques. Since little is known about the luminescence properties of the constituents of the resin, measurements were performed on the liquid base and hardener in addition to the film after polymerisation. In this way, it has been possible to study independently the species responsible for the photoluminescence in each of the constituents of the resin, before its polymerisation. Since the molecular interactions are very different from a liquid phase to a solid, important changes are expected.

The chromophores that are electrically active, i.e. that are able to trap electrical charges, are expected to be revealed in charge recombination induced luminescence (RIL). The principle of the experiment is the production of charges of both signs at the surface of the sample and the analysis of the luminescence stimulated by their radiative recombination. This can be achieved in a specially designed luminescence experiment that will be described below.

The information gathered by using these two techniques, it is thought, will provide a basis for understanding the origin and significance of EL.

2. Material and experimental

2.1.Epoxy resin

Film samples of unfilled epoxy resin were used for various experiments. A convenient resin that is polymerisable at RT has been chosen. After mixture of the base resin and hardener (100:33) the viscous liquid is poured into a mould made of carefully polished aluminium plates. The base resin is essentially composed of Diglycidyl Ether of Bisphenol-A (DGEBA) and Iso-Octyl Glycidyl Ether (IOGE) whereas the main component of the hardener is a Triethylene Tetra Amine (TETA) and polyoxypropylene with a weak percentage of salicylic acid. The formulae of the main constituents of the resin are given in Figure 1. After polymerisation the resulting films are transparent. Plastic or metallic spacers are used to prepare samples of different thickness, which can vary from 55 to 300 μm . Depending on the source of excitation, samples of different thickness were chosen and conditioned.

2.2. Experimental

Whatever the excitation source, luminescence was detected by using a photomultiplier working in photon counting mode and a monochromator coupled to a liquid nitrogen cooled CCD camera. The photomultiplier has a flat spectral response in the domain of wavelength extending from 200 nm to 900 nm. It allows the analysis of the kinetics of the luminescence decay after the excitation beam or the silent discharge has been turned off in photo- and plasma-induced luminescence (PIL) experiments respectively. The CCD camera was used in conjunction with a monochromator (Jobin-Yvon CP200 type) to analyse the spectral dispersion of the luminescence with a wavelength resolution of 4.5 nm. Acquisition of several spectra consecutively is also possible. We have used this possibility to analyse the time-dependence of the luminescence spectra during the natural decay of the phosphorescence (life time of the order of ms to s). More details on the experimental set-up can be found in [8].

2.2.1 Photoluminescence

The source of photons is a xenon lamp of 150 W that produces a continuous spectrum in the range 200-1000 nm. The lamp is coupled to an irradiation monochromator (Jobin-Yvon type H10UV with a spectral range of 220-750nm) 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.

Quartz cuvettes were used when analysing liquid components. The excitation beam is directed onto one side of the cuvette whereas the emission light is collected along a perpendicular axis. Measurements were performed at RT and atmospheric pressure. Similar measurements have been repeated on thick samples of polymerised material cut into a block of resin in order to have the same shape as the cuvette. Films were also investigated. In both case, the samples were directly irradiated with the source of photons. Both RT and LNT measurements have been performed when studying the polymerised resin. When working at LNT, the chamber was first pumped down and then filled with helium atmosphere as a thermal exchange gas.

Two kinds of spectra were recorded. The emission spectrum with its dependence on the excitation wavelength and the excitation spectrum which is obtained by recording the

variation in the amplitude of the main component of the emission spectrum as a function of the excitation wavelength.

2.2.2 Recombination Induced Luminescence

The technique used has been described elsewhere [9]. Charges of both polarities were deposited on 55 μm -thick films upon contact with a silent discharge produced in helium at atmospheric pressure between two parallel electrodes. The sample was deposited on the lower one and the upper one was a transparent indium-tin oxide (ITO) film laid on a quartz disk in such a way that the discharge was initiated between two dielectrics. The plasma gap of 5 mm was powered at a frequency of 5.5 kHz under a voltage of about 1.5 kV RMS. Before introducing the helium, the chamber was pumped down to 10 Pa (10^{-5} mbar). Experiments were undertaken at liquid nitrogen temperature for enhancing emission, and using short interaction time (5 s) for inducing negligible surface transformation. The decay of light emitted by the sample after discharge switch off was analysed in both the integral and wavelength-resolved forms. At short times, luminescence excited through processes other than radiative recombination was recorded. The analysis of the decay kinetics of integral light, i.e. the total light integrated over the complete range of wavelengths measured, allowed the unambiguous determination of the time range in which recombination was the dominant excitation mechanism. The related emission spectrum was identified accordingly. We refer to PIL (Plasma-Induced Luminescence) for the global information, irrespective of the excitation mechanism, and to RIL (Recombination-Induced Luminescence) for the part of the signal related to electric charge recombination. In the presentation of the results, reference will only be made to the emission spectra recorded in a time range where charge recombination was found to be dominant.

2.2.3 Electroluminescence

The preparation steps of the sample 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 the ill-defined field at the periphery of the metallised 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 light collection. Measurements were performed at 298 K under a pressure of 10^{-4} Pa using an AC voltage excitation.

3. Results and discussion

3.1 Photoluminescence

The response obtained from films and blocks of polymerised epoxy were identical. We will therefore not make any further reference to the kind of sample used.

3.1.1 RT experiments

Normalized emission spectra of base resin, hardener, and cured resin are shown in Figure 2. The essential features of these spectra are summarized in Table 1.

The base resin emission spectrum exhibits three emission peaks at 325, 375 and 395 nm ($\lambda_{\text{excitation}}=305\text{nm}$), whereas the hardener and cured resin produce single peaks at 405 nm ($\lambda_{\text{excitation}}=362\text{nm}$) and 410 nm ($\lambda_{\text{excitation}}=355\text{nm}$) respectively. Although the emission from the hardener and cured resin exhibit two peaks with almost the same wavelength maximum, they have different shapes suggesting they might be due to different chromophores. This is confirmed by considering the excitation spectra of these two products. It can be shown from Figure 3 that the excitation maxima are significantly different from hardener to base resin, as is the shape of the spectra. This unambiguously confirms that the luminescence of hardener and base resin could not be due to the same species

Considering the chemical constituents of the hardener, it can be seen that salicylic acid is likely to play the role of a chromophore. A literature survey of the luminescence properties of the salicylic acid shows that it indeed may behave as a chromophore, but its luminescence properties are complex. Salicylic acid is an aromatic compound possessing π , π^* and n , π^* states. Fluorescence does not usually occur in such compounds as there is an efficient intersystem crossing between singlet and triplet states leading to phosphorescence [10]. However, salicylic acid acquires a fluorescent character when it is in an ionic form [11, 12]. In fact it is believed that the acid exists before polymerisation in both mono and di-anion forms in equilibrium with the neutral form. Fluorescence at 420 nm and 410 nm has been reported for the mono-anion and di-anion respectively which is in line with the emission spectrum of the hardener. The disappearance of its emissive contribution in the cured resin is explained by a change in its chemical form

The origin of the luminescence of the cured resin can be discussed considering the excitation spectra of the base and cured resin. The excitation spectrum of the former is shown in Figure 4. An excitation spectrum has been recorded for each component of the emission spectrum. Two of them have similar shapes; this leads one to believe that the two corresponding emission peaks (375 nm and 400 nm) are due to the same chromophore whereas the other one (325 nm) might have a different origin. The important point is that the excitation spectrum of cured resin peaks at a wavelength (353 nm), which is also a maximum in the excitation spectrum of the base resin. This specific absorption gives rise to an emission at 400 nm in the liquid phase and 410 nm in the solid phase. This is consistent with the fact that in the solid phase, excimer configurations are likely to be formed because of favourable molecular interactions. The red shift of about 10 nm observed in the emission spectrum of cured resin is what can be expected for an excimeric emission [7]. The maxima at about 320 nm in the excitation spectrum of the base resin is not seen anymore after curing which is likely due to a change in the chemical form of the group responsible for this absorption. It seems that the excitation energy is channelled into a single excited state that it is responsible for the 410 nm emission of the cured resin. The identification of the chemical nature of this group is not straightforward. Usually the various spectral components of the photoluminescence are widely influenced by the environment so that the same chemical can have different emission spectra depending on the interactions with the neighbouring species, especially in polar media such as epoxy resin. Conversely, two different species can have very similar emission spectra. Due to the large number of molecular species present in the base resin, the identification of the emissive chromophores remains difficult. However, from the above analysis, it seems that the cured resin fluorescence might be due to the excitation of molecules that are already present in the base resin, but that interact differently because of the proximity of the macromolecules in the solid phase. Among these chemicals, the aromatic structures are obviously worth considering. The component that is most likely to emit light is the phenyl group provided by the Diglycidyl Ether-Bisphenol A (see Figure 1). The proximity of the oxygen atom would induce a red shift in the optical absorption relative to the one of the phenyl ring alone. However, even in the presence of this red shift, the optical absorption of the substituted phenyl ring cannot by itself explain the fluorescence observed in the cured resin [10, 12]. The features of the fluorescent emission from the base and cured resin could be due to the presence of a more conjugated species present in the chain.

The fluorescence of the bisphenol A-based epoxy resin has been reported with about the same excitation (350 nm vs. 353 nm for the present study) and emission (424 nm vs. 410 nm for the present study) wavelengths [7] as those found in our study. It was attributed to an impurity present in the amine. This is clearly not consistent with our data that shows that the fluorescence of base resin has a different origin to that of the hardener.

Further information regarding the origin of resin luminescence might be collected in low temperature measurements reported below.

3.1.2 LNT experiments

Measurements performed on the cured resin at LNT give access to complementary information. The emission spectrum is shown in Figure 5. The emission peak at 412 nm is the fluorescence emission already detected at RT whereas the broad emission peaked at about 500 nm is interpreted as a phosphorescence component. Superposition of the fluorescence peak detected at RT shows that the later is weakly temperature dependent. Further confirmation of the phosphorescent nature of the emission peak at 497 nm is obtained by a kinetic analysis of the spectral shape carried out after switching off the excitation beam. As shown in Figure 6, the emission spectrum can be resolved in time during the natural decay of the phosphorescence (i.e. different spectra were recorded consecutively immediately after excitation beam switch-off) whereas there is no trace of the fluorescence in agreement with its short lifetime (order of 10^{-8} s). Three components have been detected at 450, 510 and 550nm. It is clearly seen from the different decay kinetics of these peaks that at least two and possibly three different chromophores are contributing to the phosphorescence emission. As for fluorescence emission, the assignment of the phosphorescence components to given chemicals is not straightforward. It is first necessary to establish whether one of the fluorescent species could also be responsible for a component of the phosphorescence. This can be checked by analysing the excitation spectra (not shown) monitored at 450 nm and 510 nm. Although it is difficult to separate these two components because of the overlapping of their phosphorescence spectra, the excitation of the 450 nm peak is effective in the range of excitation of the fluorescence (350 nm) 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 species that does not give a fluorescence emission.

The phosphorescence of Bisphenol-A epoxy resin has been reported [7] 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 [7]. The results obtained in our study allow the fluorescence at 410 nm and phosphorescence at 450/460 nm to be attributed to the singlet and triplet excimer of a chromophore that is part of the polymer chain.

3.2 Recombination-Induced Luminescence

The time-dependence of the luminescence recorded 1 s after the end of the plasma discharge is shown in Figure 7. The experimental data have been fitted by a function that takes into account the different processes that contribute to the luminescence excitation [9].

$$3.29 \times 10^5 e^{-t/6.64} + 9.82 \times 10^5 e^{-t/1.44} + 1.37 \times 10^5 / (1 + 0.3816t) \quad (1)$$

For the purpose of this study, the important point is to define the time range where charge recombination is the main contributing process. This regime is clearly defined from Figure 7 since charge recombination-induced luminescence fits an hyperbolic law in time and appears therefore as a straight line in a double logarithmic plot. This regime is found for times, $t > 20$ s. The emission spectrum due to charge recombination can therefore be acquired if the integration of the luminescence is initiated for times greater than 20 s. A typical spectrum obtained in this time range is shown in Figure 8. It is clear that it is organized around the same components as the photo-induced phosphorescence emission of the resin, although their relative contributions are 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 also play the role of recombination centres.

More interestingly, it is also found that fluorescence is not excited during charge recombination. This behaviour has been found in all the polymeric materials studied so far [13, 14]. The absence of fluorescence in recombination-induced luminescence can be explained in various ways. For example, if a fluorescent chromophore is not associated with a pronounced affinity for charge carriers, it will not act as a recombination centre and will not be excited upon charge recombination. On the other hand, even if a chromophore does act as a

recombination centre, it may simply not be an efficient fluorescence centre. Finally, for a chromophore that is a recombination centre and that can give both fluorescence and phosphorescence, there might be some reasons to have specific excitation of the triplet state relative to the singlet state. For example, Kalinowski [15] expressed the probability of forming a singlet exciton in a recombination process as:

$$\alpha = \frac{1}{4} \exp\left\{-\frac{E_s - E_t}{kT}\right\} \quad (2)$$

where E_s and E_t represent the energies of the first excited singlet level of the recombination centre and the trap. Thus when $E_s \gg E_t$, α tends toward zero, only triplet states are created. The epoxy resin under study is an interesting example for discussion of this question. Our experimental results allowed the fluorescence at 410 nm and phosphorescence at 450/460 nm to be associated to the same chromophore. The absence of fluorescence in charge recombination would mean that the trapping level is located in between the singlet and triplet state of the recombination centre, promoting a selective excitation of the phosphorescence of the chromophore.

3.3 Electroluminescence

AC electric fields of 21 kV/mm and 35.7 kV/mm produced different spectra, using an integration time of 10 min, Figure 9. The spectrum recorded at 21kV/mm gives one peak at 593nm whereas the spectrum recorded at the higher field shows the same peak and two additional shoulders. A fit by using Lorentzian functions has been used for the spectrum corresponding to the higher field. This results in decomposition into 3 functions described by equation 3:

$$EL(\lambda) = \sum_{i=1}^3 \frac{2A_i\omega_i}{\pi} \frac{1}{\omega_i^2 + 4(\lambda - \lambda_{p_i})^2} \quad (3)$$

The characteristics of peak i are: the area A_i , the half-width ω_i , and the wavelength λ_{p_i} . Values of the fitting parameters are given in Table 2. When compared with the spectrum due to charge recombination, a common structure appears at 435 nm and 541 nm. This component could therefore be due to the recombination of charges. Charge-recombination is expected to occur in electroluminescence if the excitation involves impact-ionisation by hot carriers or bi-

polar injection. In both cases, thermalised carriers are generated after the ionisation events or the injection respectively. As a consequence, there will be 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 595nm has never been observed from other kinds of luminescence excitation. It is clearly located in the wavelength domain of phosphorescence and might be another phosphorescent component probably associated with the degradation of the material. Electroluminescence therefore involves relaxation of excited states through irreversible pathways, which link the emission and the deterioration of the resin. Further investigations are needed to give definitive evidence of this finding.

4. Conclusions

The luminescence properties of bisphenol-A type epoxy resin have been investigated to lend support to the interpretation of the electroluminescence, which is thought to be linked to the electrical ageing and breakdown mechanisms. 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, it has been shown that the recombination centres in the cured resin are part of 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. This could be due to the energy level of the trapping centres that lies in between the first excited singlet and triplet states of the recombination centre. The emission spectrum of electroluminescence is also located in the phosphorescence region, but its form cannot be completely explained by the recombination spectrum; there is another component of the electroluminescence emission that could be related to the molecular degradation of the resin. Although further investigation is needed to understand better the relationship between the luminescence properties of the resin and the ageing process, this work will enhance the comprehension of electroluminescence in this material.

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FIGURE CAPTIONS

Table 1 : RT photoluminescence features for base resin, hardener and cured resin

Table 2 : Fitting parameters of the electroluminescence spectrum recorded at 35.7 kV/mm

Figure 1 : Chemical formulae of the main constituents of the epoxy resin

(a) Components of the base resin

(b) Components of the hardener

Figure 2 : Normalized RT photoluminescence spectra of base resin (solid line, $\lambda_{exc}= 305$ nm), hardener (doted line, $\lambda_{exc}= 362$ nm), and cured resin (dashed line, $\lambda_{exc}= 355$ nm)

Figure 3 : Normalized excitation spectra for the hardener (doted line, $\lambda_{em}= 405$ nm) and cured resin (dashed line, $\lambda_{em}= 410$ nm)

Figure 4 : RT photoluminescence excitation spectra for the base resin recorded at

□ : $\lambda_{em}= 325$ nm; ▽ : $\lambda_{em}= 375$ nm; • : $\lambda_{em}= 400$ nm

Figure 5 : RT (dashed line) and LNT (full line) photoluminescence emission spectrum for the cured resin for $\lambda_{exc}= 350$ nm

Figure 6 : Phosphorescence decay spectra of cured resin. Spectra recorded every 0.5 s, (excitation wavelength of 320 nm)

Figure 7 : Luminescence decay after plasma discharge switch-off. The dashed line is the contribution of recombination induced luminescence to the total signal. It dominates after 20 s in the decay.

Figure 8 : Emission spectrum due to charge-recombination (thick line), Normalized LNT photoluminescence spectra recorded at different excitation wavelengths 0.5 s after the end of the excitation (thin line : $\lambda_{exc}= 280$ nm, dashed line : $\lambda_{exc}= 320$ nm, doted line : $\lambda_{exc}= 360$ nm)

Figure 9 : (a) Electroluminescence spectra at two different fields (ac voltage) 50 Hz

(1) 21 kV/mm, (2): 35.7 kV/mm

(b) Fit of spectrum (2) to equation 3. Dashed lines are the decomposed peaks.

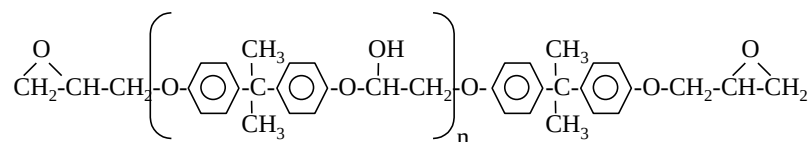
Table 1 : RT photoluminescence features for base resin, hardener and cured resin

Component	$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{emission}}$ (nm)
Base resin CY1301	305	325, 375, 400
Hardener HY 1300	362	405
Cured resin	355	410

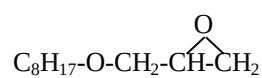
Table 2 : Fitting parameters of the electroluminescence spectrum recorded at 35.7 kV/mm

Component	1	2	3
λ_p (nm)	435	541	597
ω (nm)	51	64	208
A (counts.nm)	1168	1333	19895

(a) Components of the base resin

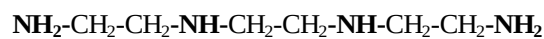


Diglycidyl Ether-Bisphenol A

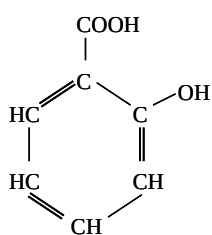


Iso-Octyl Glycidyl Ether

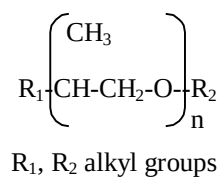
(b) Components of the hardener



Triethylene Tetra Amine



Salicylic Acid



Polyoxypropylene

Figure 1 : Chemical formulae of the main constituents of the epoxy resin

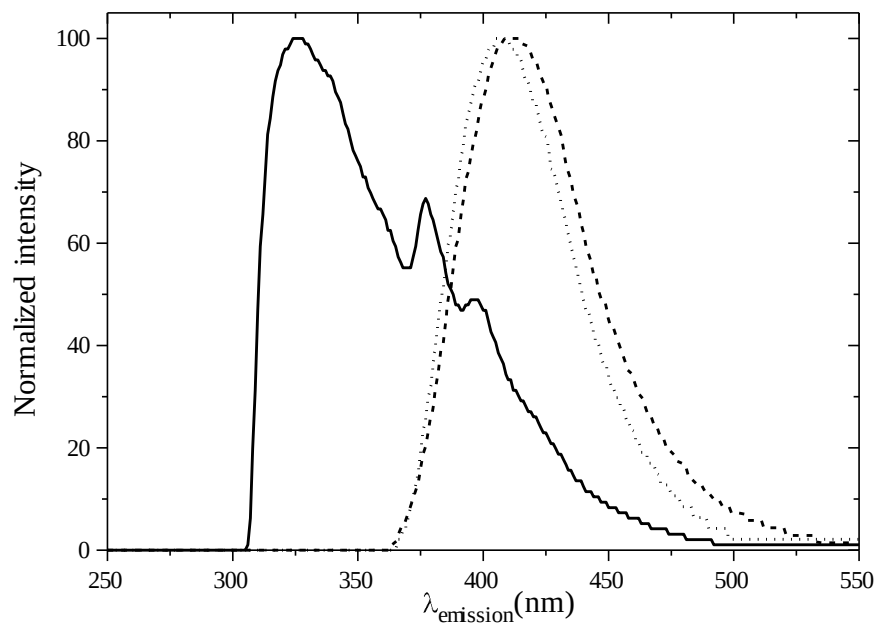


Figure 2 : Normalized RT photoluminescence spectra of base resin (solid line, $\lambda_{\text{exc}} = 305$ nm), hardener (dotted line, $\lambda_{\text{exc}} = 362$ nm), and cured resin (dashed line, $\lambda_{\text{exc}} = 355$ nm)

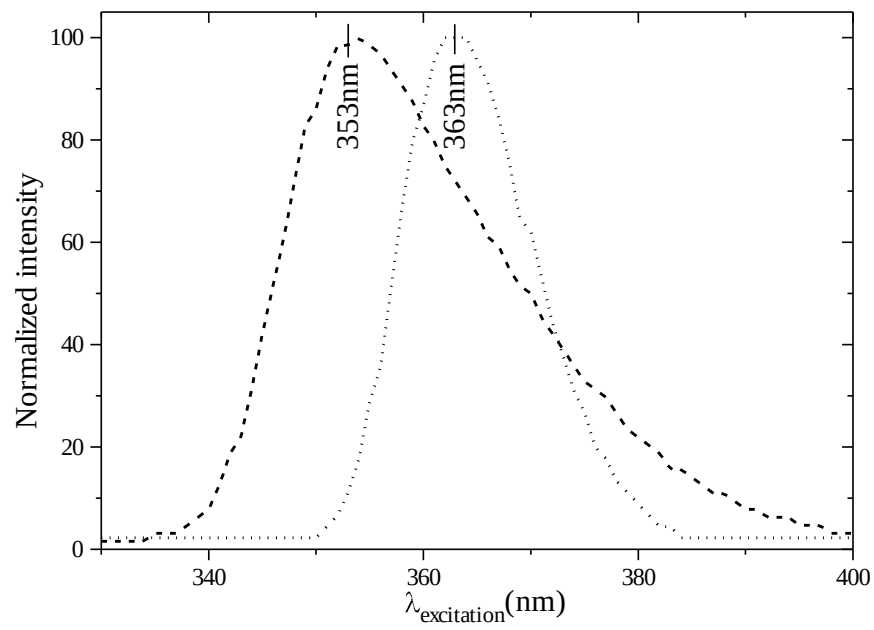


Figure 3 : Normalized excitation spectra for the hardener (doted line, $\lambda_{\text{em}}= 405$ nm) and cured resin (dashed line, $\lambda_{\text{em}}= 410$ nm)

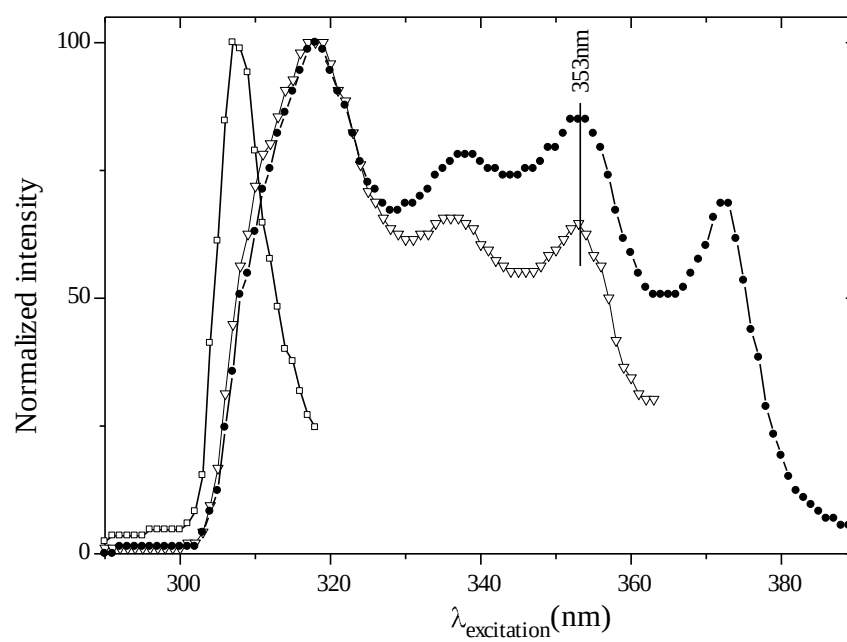


Figure 4 : RT photoluminescence excitation spectra for the base resin recorded at

$\square$: $\lambda_{\text{em}} = 325$ nm; ∇ : $\lambda_{\text{em}} = 375$ nm; $\bullet$: $\lambda_{\text{em}} = 400$ nm

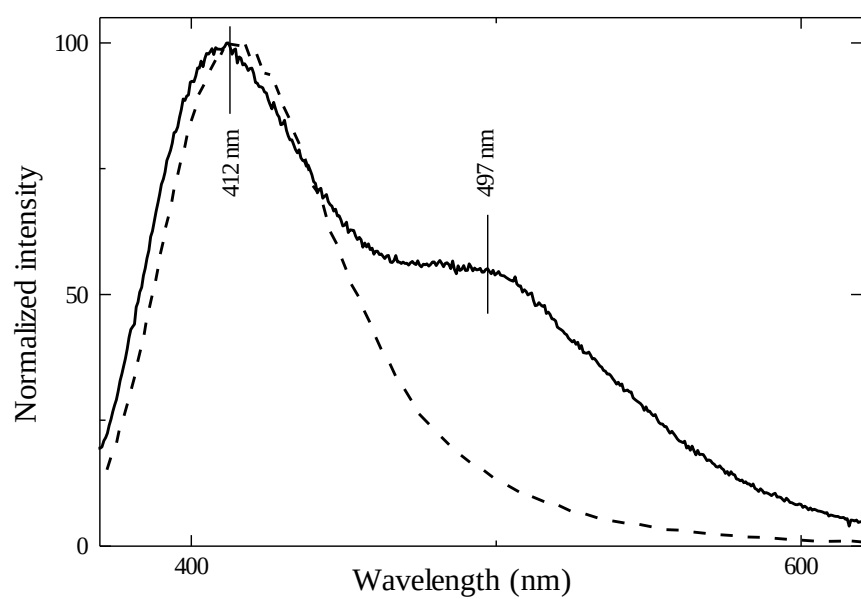


Figure 5 : RT (dashed line) and LNT (full line) photoluminescence emission spectrum for the cured resin for $\lambda_{\text{exc}} = 350 \text{ nm}$

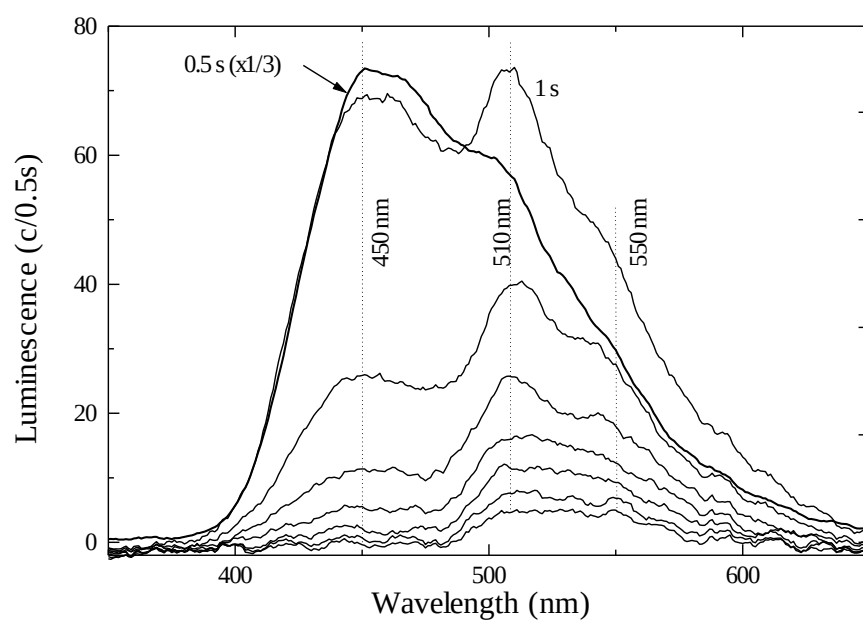


Figure 6 : Phosphorescence decay spectra of cured resin spectra recorded every 0.5 s,
(excitation wavelength of 320 nm)

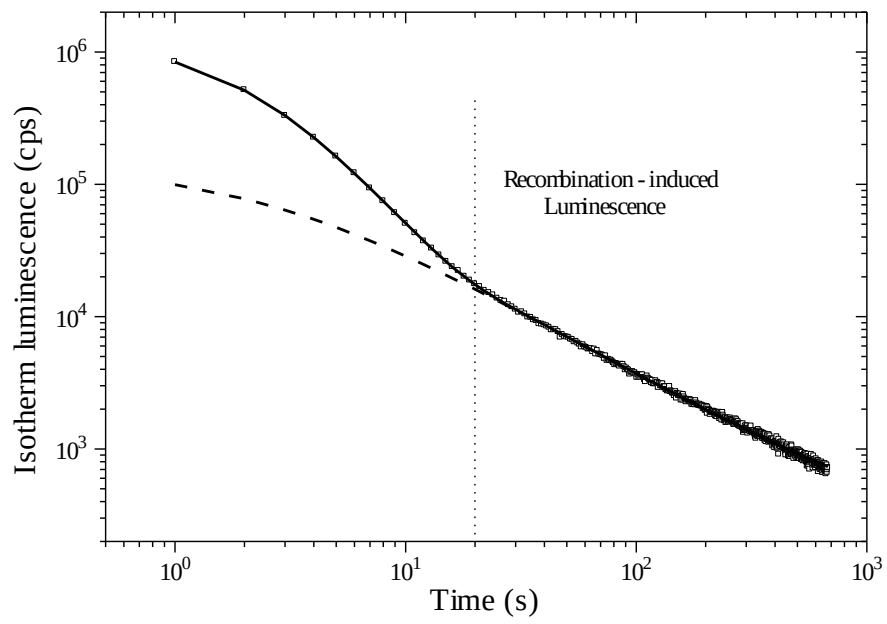


Figure 7 : Luminescence decay after plasma discharge switch-off. The dashed line is the contribution of recombination induced luminescence to the total signal. It dominates after 20 s in the decay.

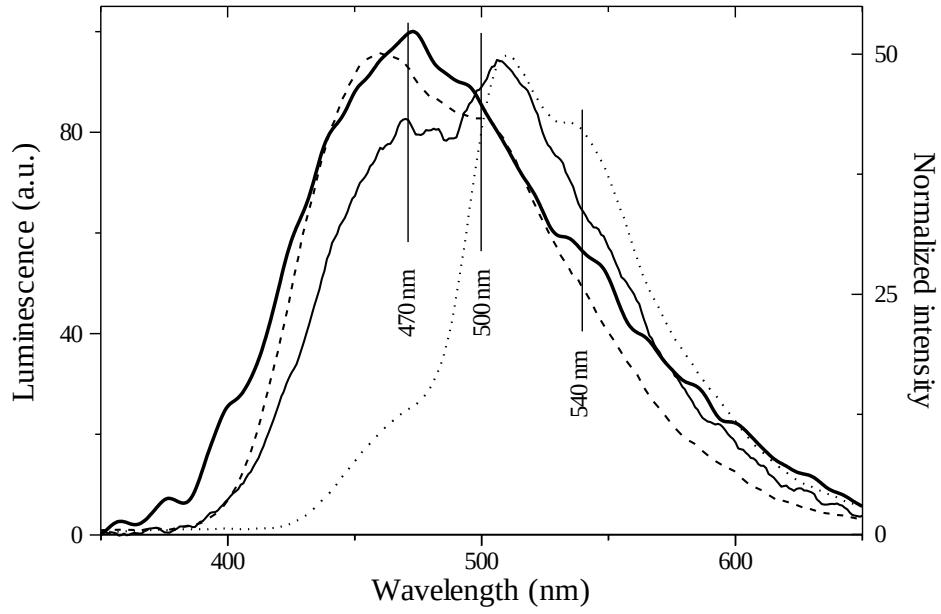


Figure 8 : Emission spectrum due to charge-recombination (thick line), Normalized LNT photoluminescence spectra recorded at different excitation wavelengths 0.5 s after the end of the excitation (thin line : $\lambda_{\text{exc}} = 280$ nm, dashed line : $\lambda_{\text{exc}} = 320$ nm, dotted line : $\lambda_{\text{exc}} = 360$ nm)

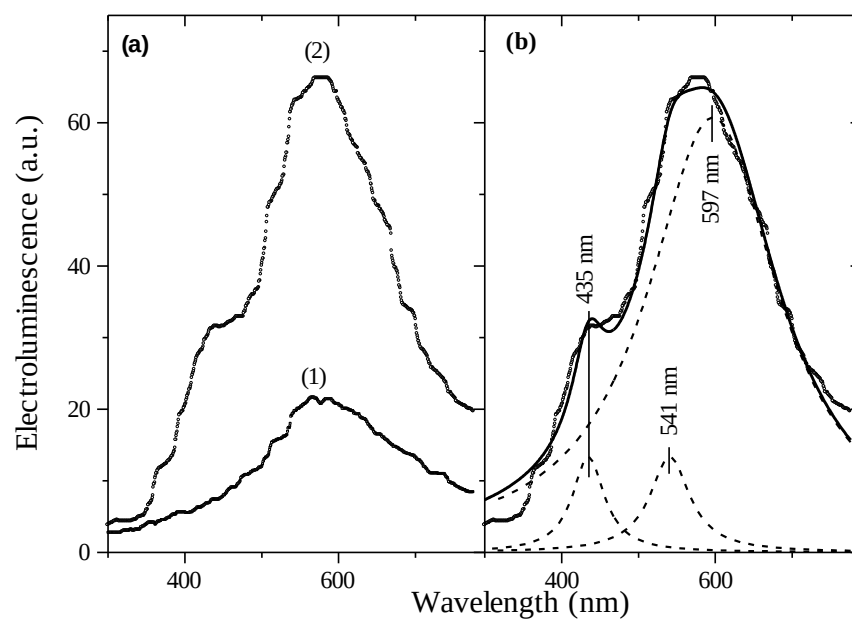


Figure 9 : (a) Electroluminescence spectra at two different fields (ac voltage) 50 Hz

(1) 21 kV/mm, (2): 35.7 kV/mm

(b) Fit of spectrum (2) to equation 3. Dashed lines are the decomposed peaks.