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# Chemiluminescence Monitoring During an Epoxy Curing Reaction

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## Abstract-

Chemiluminescence is one of the ways to monitor chemical reactions, and notably the curing of epoxy resins. The kinetics and conversion of the reaction are classically monitored using total light emission without consideration of the emission spectrum. In the present work, we investigated the chemiluminescence of an imidazole catalyzed epoxy resin during its curing at 90°C. Attention is paid to the change in the chemiluminescence spectrum with the extent of the reaction. The spectral distribution changes with curing time and exhibits a non-monotonous behavior that correlates well with the chemiluminescence intensity monitored with a photomultiplier. The curing chemiluminescence is attributed to the oxidation of the material in an evolving environment and is promoted by the exothermicity of the curing reaction. After a short period of time where only the oxidation of the catalyst and the hardener are revealed, the reaction rate accelerates and peaks after 40 min of curing at 90°C. Then, the chemiluminescence spectrum progressively evolves toward the one characteristic of the fully cured resin. This study demonstrates that analyzing the spectral distribution of luminescence can effectively determine the curing reaction stage of a given resin.

**Keywords-** chemiluminescence, epoxy resin, imidazole, curing reaction, oxidation

## I. INTRODUCTION

Epoxy resins are thermoset polymers widely used in electrical insulation, as adhesives, coatings, and encapsulating medium of electronic circuits, owing to their excellent mechanical and electrical properties and their chemical and thermal stability [1]. These crosslinked epoxy networks can be synthesized using a large variety of hardeners, including diamines, anhydrides, phenols, etc.; and catalysts, such as, imidazoles, triamines, metallic complexes, etc. [2]. Imidazole catalysts are particularly noteworthy thanks to their high reactivity which induces homopolymerization of epoxy resins and enable rapid curing at relatively low temperatures, (about 100 °C or below), with catalyst concentration of typically 10 wt % or less [3].

In a recent study, we observed that an imidazole catalyzed epoxy resin was able to emit weak but noticeable luminescence under coupled mechanical and thermal stresses, so called mechanoluminescence. This phenomenon was attributed to thermo-mechanical bond scissions in the network, followed by luminescent chemical reactions with oxygen [4]. In order to investigate the nature of the excited states responsible for the observed light emission in mechanoluminescence, correlations with other routes of exciting light need to be investigated. In the present work, we report the chemiluminescence behavior of this resin upon curing.

Chemiluminescence (CL) is the emission of light following chemical reactions. It can be emitted by a material when an excited product formed by an exoenergetic chemical reaction decays radiatively to its ground state [5]. The energy of the emitted photons is a signature of the excited molecular groups. This phenomenon can typically happen following oxidative reactions with oxygen, and has been observed for many thermoplastic polymers, the most studied in the literature being polypropylene (PP) [6,7]; as well as some epoxy resins which can show significant light emission [8–10]. Chemiluminescence has also been used to study the curing reaction of some epoxy-diamine resins, through the indirect monitoring of oxidative reactions during the curing process [11,12]. It was shown that the curing-chemiluminescence can reflect the extent of the reaction by comparing it to FTIR and calorimetric techniques. A maximum of luminescence was observed which was correlated with the gel time determined in rheology experiments. However, wavelength-resolved chemiluminescence spectra during the curing reaction were never reported and the precise mechanism behind this phenomenon remains unclear.

This article describes the chemiluminescence of a commercial epoxy-imidazole resin. The CL, observed only in air, necessarily results from oxidation reactions. The CL of the resin is first analyzed in terms of its two compounds taken separately. The curing reaction is then monitored to explain the differences observed between the steady state chemiluminescence spectra of the cured resin and its constituents and potential emissive chemical groups are identified. Through combined temporal and spectral measurements, a deeper understanding of the nature of the curing chemiluminescence is provided, notably by considering the role of the exothermicity of the reaction. More generally, the potentiality of the method to monitor exothermic reactions is demonstrated.

## II. EXPERIMENTAL

### A. Material

The chemiluminescence of a commercial epoxy resin (Polytec EP 630), with the chemical composition provided in Fig. 1, was investigated. It is obtained from the reaction of two components: an epoxy resin (part A), and a catalyst and a monofunctional molecule (part B). The epoxy resin consists of two diepoxides, Bisphenol F diglycidyl ether (BFDGE) for the most part, and 1,4-Butanediol diglycidyl ether (BDDE) in low weight fraction. The second

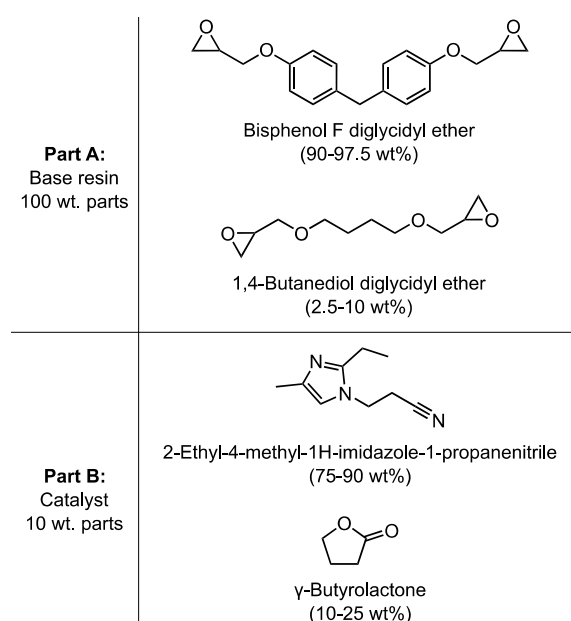


Fig. 1. Chemical compositions of compounds used in the formulation of the resin.

component is composed of a catalyst, 2-Ethyl-4-methyl-1H-imidazole-1-propanenitrile (EMIP), and a monofunctional molecule, i.e.  $\gamma$ -Butyrolactone in low weight fraction. This resin has a moderate glass transition temperature of about 120 °C. To prepare 300  $\mu\text{m}$ -thick disks with a diameter of 4 cm, parts A and B were mixed in a 100:10 weight ratio using a planetary mixer under vacuum (10 mbar). Except otherwise stated, all luminescence experiments were realized on resin samples of same shape and volume. The mixing process involved stirring at 800 rpm for 3 minutes, followed by 1800 rpm for 1 minute, ensuring complete homogeneity of the material and preventing the formation of air bubbles. The mixture was then poured into a Teflon mold and cured at 100 °C for 1 h in a hot press, and then immediately placed in an oven at 120 °C for 2 h to finish the curing process.

### B. Chemiluminescence detection

The experimental setup for chemiluminescence detection is described in Fig. 2. In a light proof chamber, samples are set on a brass heater that can control the temperature between room temperature (RT) and 175 °C. Temporal detection of the luminescence can be performed using a photomultiplier (PM) in counting mode (R943-02, Hamamatsu) cooled to -30 °C to reduce the thermal background noise to less than 1 count per second (cps) in average. Dwelling time for photon counting was always set to 1 s in this study. Spectra can also be acquired with this setup using a CCD camera (Spectrum one D-91, Jobin-Yvon) cooled to -130 °C coupled to a diffraction grating (CP200 – 133g/mm, Jobin-Yvon). The entrance slit was chosen with a width of 2 mm to balance between resolution and signal intensity. With this slit, a 15 nm resolution is achieved. To switch between temporal and spectral measurements, a 45 ° angled mirror can be pushed to deviate the light emitted by the sample towards the CCD camera. A set of three lenses ( $L_1$  to  $L_3$ ) is used along the optical axes to focalize the light either on the photocathode of the PM or on the CCD camera. The chamber can be evacuated to either a primary or secondary vacuum and the atmosphere can be air or nitrogen.

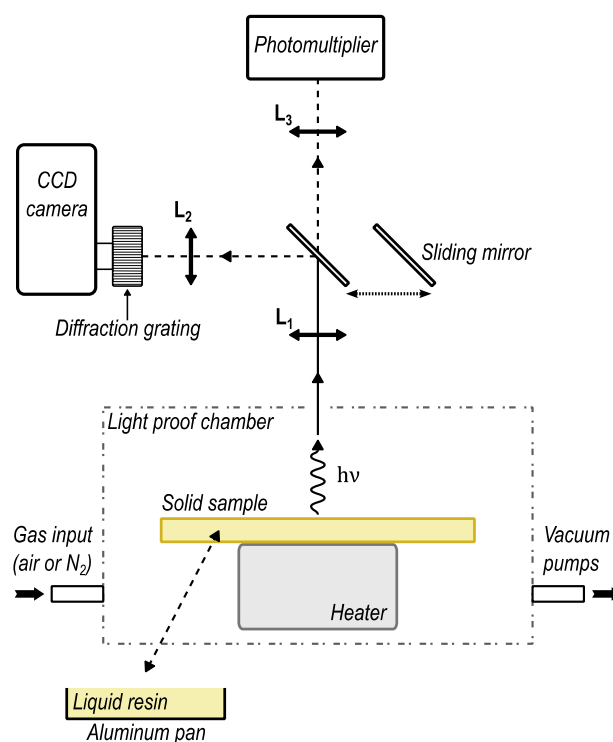


Fig. 2. Representation of the setup used for chemiluminescence detection of samples both liquid (both parts alone or during curing) or solid (cured).  $L_{1,2,3}$  refer to the lenses used for luminescence collection.

Both flat solid samples and liquid samples placed in an aluminum pan can be studied using this setup. Studying epoxy resins in a liquid state (i.e. before curing) is particularly interesting to monitor the chemiluminescence during the curing reaction. Chemiluminescence of the pure liquid resin or the liquid catalyst can also be investigated separately in this way.

### C. Other characterization methods

The **gel time** of the epoxy resin was determined using a MCR 302 Anton Paar shear stress rheometer. Oscillatory measurements using parallel plates of 25 mm in diameter with a gap of 1 mm, an angular velocity of 1 rad/s and a strain of 1 % were performed at three different frequencies of 1, 5, and 10 Hz. The gel point was taken at the intersection between the three  $\tan(\delta)$  curves obtained for the three frequencies according to the Winter-Chambon criterion [13].

**Differential Scanning Calorimetry (DSC)** analyses were conducted with a Mettler Toledo Differential Scanning Calorimeter under a constant nitrogen flow rate (50 mL/min) on samples of about 3-6 mg at different isotherms to monitor the curing reaction, followed by a temperature ramp at 10 °C/min up to 175 °C to detect unreacted parts.

## III. RESULTS

### A. Chemiluminescence spectra of parts A and B compared to the crosslinked resin

The cured resin emits an intense chemiluminescence when heated in air, whereas no signal is recorded in nitrogen. This behavior is typical of epoxy resins [10,14,15] and was partly reported for this specific composition in a previous study [4]. CL in air was seen to follow an Arrhenius law between 50 and 120 °C with an activation energy of roughly 35 kJ/mol. Fig. 3a shows the spontaneous luminescence signal of the cured resin in air and in nitrogen when heated from RT (20 °C) to 100 °C during two consecutive heating runs. In these heating runs, 100 °C was reached within approximately 15 minutes. Between the runs, the samples were kept at  $5 \cdot 10^{-3}$  mbar, for the time needed for the system to cool down to RT. During the first runs, in air and in nitrogen, an intense maximum of luminescence is observed after 12-14 min. The signal then decreases and stabilizes at around 1000 cps in air, whereas in nitrogen the signal is almost completely killed, with 25 cps in average after 1 hour of heating. In the second run,

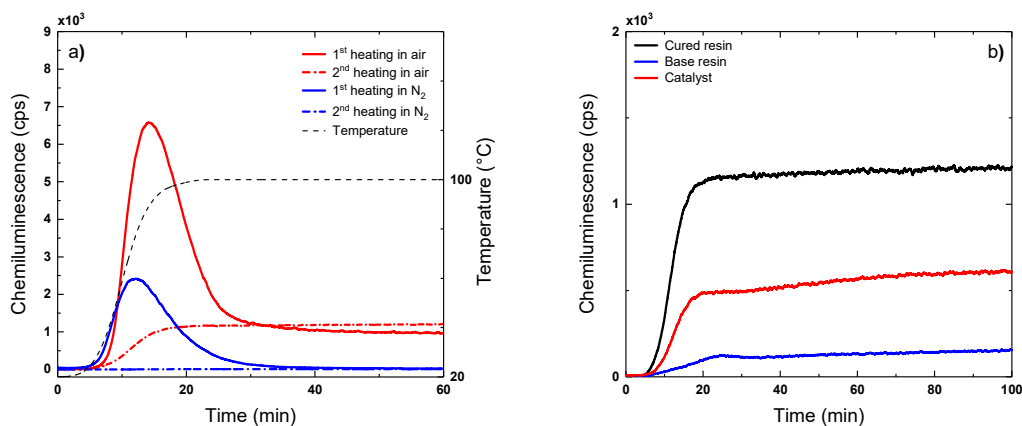


Fig. 3. a) Chemiluminescence of the cured epoxy resin in air and in N<sub>2</sub> at 1 bar heated from RT to 100 °C during the first and second consecutive heating runs. Between the runs, for the time needed for the system to cool down to RT, samples were kept at  $5 \cdot 10^{-3}$  mbar to remove oxygen and stop oxidation. b) Spontaneous chemiluminescence in air of the cured resin during the second heating run compared to the catalyst and the base resin when heated from RT to 100 °C.

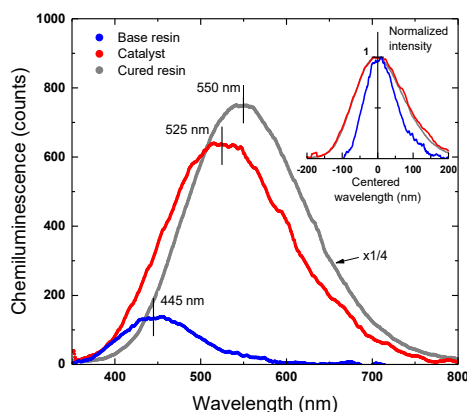


Fig. 4. Spectral distribution of the chemiluminescence of the base resin, the catalyst and the cured resin in air at 90 °C. The integration time of the CCD camera was set to 30 min. The inset graph represents the same spectra normalized in intensity and centered around their maxima where it can be seen that the CL of the cured resin and the catalyst are almost overlapping.

in air, no maximum is observed and the signal increases to a similar but slightly higher plateau compared to the first run. In nitrogen, a very weak chemiluminescence of about 10 cps in average is recorded. The bell shape and the presence of a maximum during the first runs have been attributed to diffusion controlled substances already present in the material prior to heating [14], notably oxygen initially dissolved into the material. These substances are eliminated upon heating the first time, and thus the luminescence peak is not observed in following runs if only a minimal quantity of oxygen is absorbed by the sample between the runs.

The spontaneous chemiluminescence of the base resin and the catalyst is compared to that of the cured resin in Fig. 3b. It is observed that the cured resin exhibits a significantly higher chemiluminescence intensity than its two components when considered separately. This result already suggests the presence of distinct molecular groups responsible for luminescence in the cured resin, the catalyst, and the epoxy resin.

To try to identify the luminescent centers at the origin of the observed spontaneous luminescence, emission spectra of the base resin and the catalyst were acquired at 90 °C in air with an integration time of 30 min (Fig. 4). Spectra of both parts taken separately clearly differentiate from the spectral distribution of the cured resin, which is centered around 550 nm. The uncured resin shows a weak luminescence centered around 445 nm. The catalyst is much more emissive, with an emission centered around 525 nm. When normalized and centered, the spectra of the catalyst and the cured resin match almost perfectly (Fig. 4, inset). This likely indicates that the molecular groups at the origin of light emission in the cured resin are similar to those in the catalyst, but in a changed environment. This changing environment would be the result of the crosslinking reaction.

#### B. Monitoring crosslinking with chemiluminescence

To follow the change in spectral distribution during crosslinking, and by doing so, the change in the environment of the emissive molecular groups, the chemiluminescence of the resin was monitored during the curing reaction. To do so, the temperature of the sample holder was first set to the desired temperature. About 3 g of a (liquid) mixture of base resin and catalyst, at a 100:10 weight ratio was then placed in an aluminum pan. The two parts were mixed at room temperature and placed only at the last minute on the heater inside the chamber. The chamber was sealed as quickly as possible, within one minute, to be able to monitor the onset of the crosslinking reaction.

Chemiluminescence during the curing reaction, when measured with the PM, shows a peak whose magnitude and position in time depend on the curing temperature (Fig. 5a). The peak intensity increases with temperature, whereas its width decreases and its maximum is observed at shorter times. In order to balance between sufficient signal intensity and time resolution, the chemiluminescence of the resin during the curing reaction has been studied

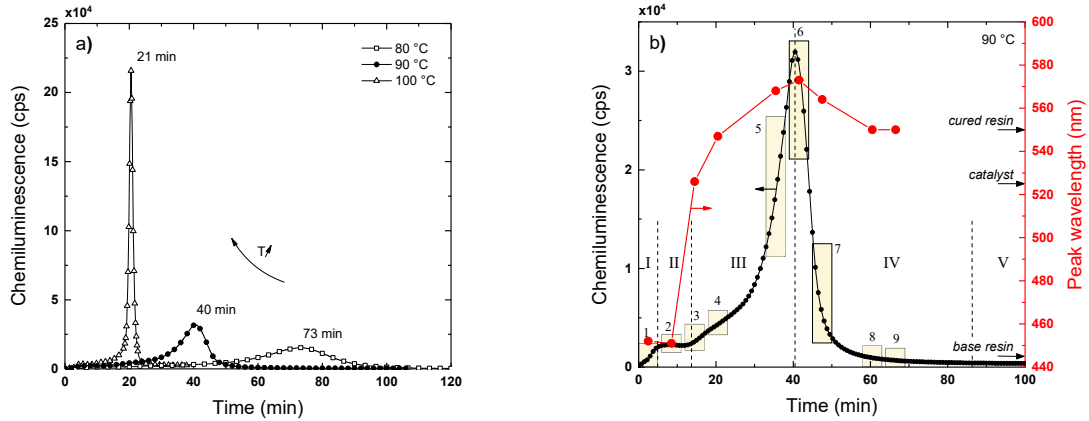


Fig. 5. a) Chemiluminescence during the curing reaction at different temperatures. b) Chemiluminescence during crosslinking (in black) of the resin at 90 °C in air. The response is separated in five different domains indicated as I to V. Colored rectangles indicate the time windows of the nine spectra realized during curing. In red is represented the change in the peak wavelength  $\lambda_{\max}$  during the curing reaction.  $\lambda_{\max}$  of the base resin, the catalyst and the cured resin are indicated as a reference.

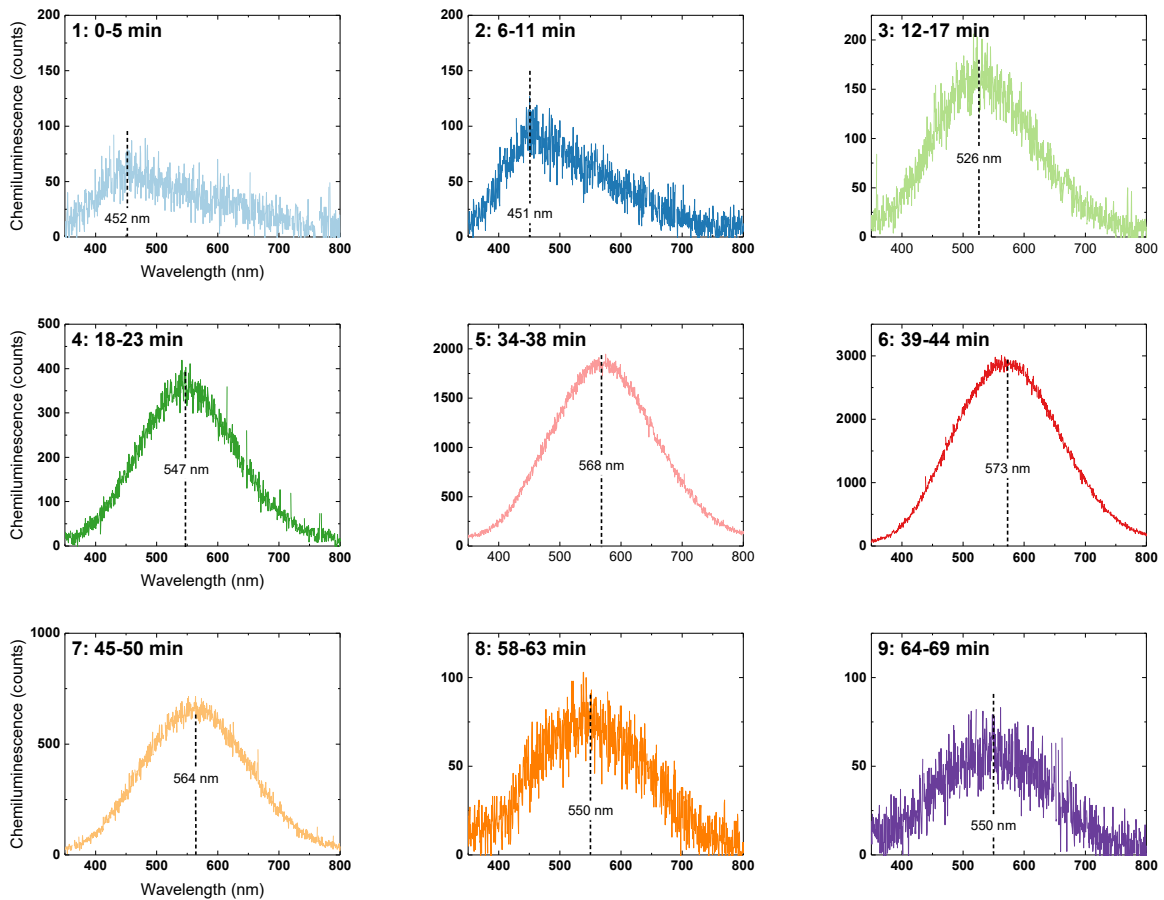


Fig. 6. Evolution of the spectral distribution of chemiluminescence during the curing reaction at 90 °C in air. The spectra are numbered and correspond to the investigation windows shown in Fig. 5.

spectrally at 90 °C. At this temperature, when measured with the PM, five different domains in luminescence intensity can be identified as shown with the black curve in Fig. 5b. During the first 5 min (domain I), the luminescence signal increases slightly from 0 (the value at RT) to roughly 2000 cps. The luminescence then shows a plateau for about 10 min (domain II). The CL intensity then increases in domain III until it reaches a very intense maximum of around 33000 cps at about 40 min. After this maximum, the CL intensity decreases (domain IV) until it reaches a constant plateau (domain V) that corresponds to the spontaneous luminescence intensity of the cured resin. Spectra of 5 min of integration were also acquired during the curing reaction of another sample. Their time windows are indicated by colored rectangles in Fig. 5b. All nine spectra are given in Fig. 6.

The spectral distribution of chemiluminescence changes as the crosslinking reaction advances. The first two spectra, acquired respectively from 0 to 5 and 6 to 11 min, are very asymmetrical and present a peak at a wavelength  $\lambda_{\max}$  of around 450 nm. The following spectra are much more symmetrical, and the center of the spectral distribution is progressively redshifted towards 573 nm in spectrum 6 (39 to 44 min).  $\lambda_{\max}$  then decreases, to finally stabilize at around 550 after an hour in spectra 8 and 9, where the spectral distribution matches that of the fully cross-linked resin (centered around 550 nm). The red curve in Fig. 5b shows the change in  $\lambda_{\max}$  with time compared to the CL intensity. Strong similarities can be observed between  $\lambda_{\max}$  and CL intensity. Similar to the CL intensity,  $\lambda_{\max}$  exhibits a plateau during the first 10 to 15 min. A very fast change is then observed between spectra 2 and 3 and  $\lambda_{\max}$  shows a maximum between 39 and 44 min, which can be correlated with the maximum of CL intensity after 40 min. After approximately 60 min, the spectral distribution reaches a steady state, which correlates well with the plateau of CL intensity observed at the same time at the end of the curing reaction.

A double Gaussian function (Eq. 1) was used to fit spectrum 2 of Fig. 6:

$$CL(\lambda) = \sum_{i=1}^2 A_i \exp\left(\frac{-(\lambda - \lambda_{\max_i})^2}{b_i^2}\right) \quad (1)$$

where:  $A_i$  and  $b_i$  are shape parameters and  $\lambda_{\max_i}$  is peak wavelength of the  $i^{\text{th}}$  peak. The result, shown in Fig. 7, highlights the contribution of two components in the spectrum, the first one being centered around 447 nm and the second one around 533 nm. It is very noteworthy that the fitted values of  $\lambda_{\max}$  obtained for the two convoluted

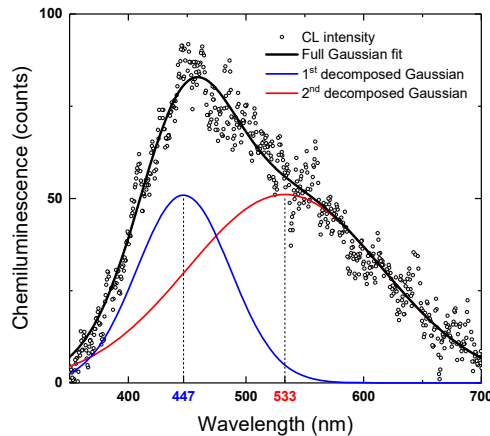


Fig. 7. The double Gaussian function fit applied on the CL spectral distribution observed between 6 and 11 min of curing at 90°C, which corresponds to the second spectrum shown in Fig. 6.

peaks after 11 min of curing correspond really well to the experimental values of the base resin and the catalyst, respectively being 445 and 525 nm.

All experiments were repeated in a nitrogen atmosphere and no luminescence could be observed. This clearly shows that it is chemical reactions between the curing resin and the ambient oxygen that allows to monitor the extent of the curing reaction using chemiluminescence. Note that a resin previously cured in nitrogen emits when heated in air with a spectrum peaking at 550 nm, similar to the one of the resin previously cured in air.

#### IV. DISCUSSION

##### A. Crosslinking mechanism

In order to discuss the luminescence processes involved during the curing of the selected resin, we first review the mechanisms currently admitted for the curing reaction. The crosslinking mechanism accepted in the literature [16–18] is given in Fig. 8. The imidazole compound acts as a catalyst to start the homopolymerization of the epoxy resin. The nitrogen in 3<sup>rd</sup> position of the imidazole compound reacts with the epoxy group, forming a 1:1 adduct. In 1-unsubstituted imidazoles, i.e. when the nitrogen in 1<sup>st</sup> position is bonded to an hydrogen atom, OH 2:1 adducts can be produced, but it is not the case for the system considered in this study, and only the O<sup>-</sup> adduct is formed [18]. Once a 1:1 adduct is formed, etherification of the O<sup>-</sup> and another epoxy group occurs. The chain growth polymerization is then conducted from this negative charge. A 3D cross-linked network is formed because each epoxy group can react twice, meaning that at 100% conversion, every BFDGE monomer will have reacted four times. Both the 1-1 adduct and the imidazole compound can be regenerated during the curing reaction, generally at high curing temperatures, and are able to initiate new reactions [3,16]. The imidazole regeneration can be achieved through *N*-dealkylation of the nitrogen substituents, which is the most likely pathway, or by Hofmann elimination. The curing reaction rate is dependent on the adduct concentration. An induction period of 15 to 20 min has been observed in several studies using FTIR [16,19]. It has been interpreted as the time needed for sufficient adduct formation to initiate the homopolymerization of the epoxy resin.

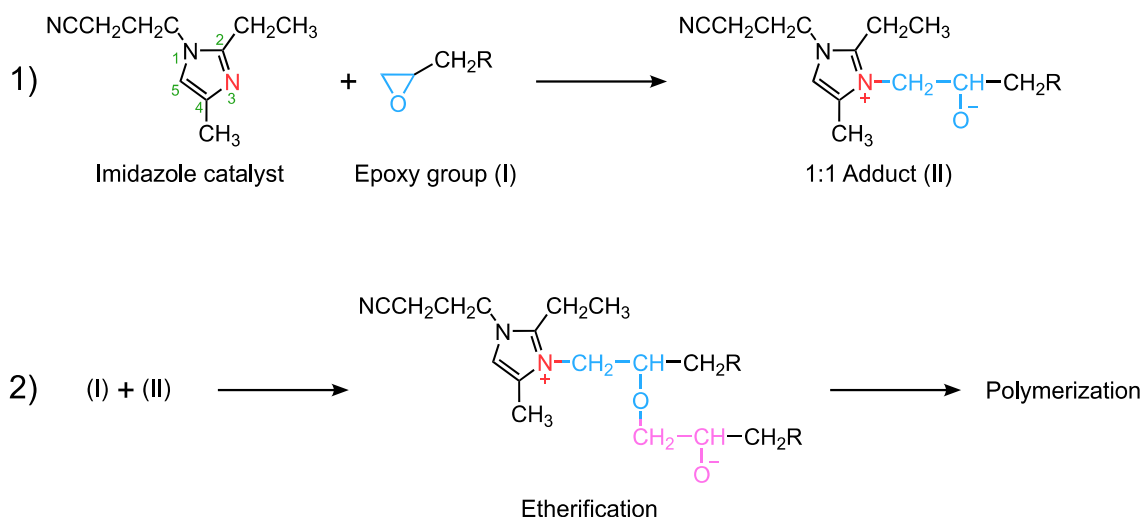


Fig. 8. Reaction scheme of the curing reaction of EMIP and an epoxy resin. The first step consists of the 1:1 adduct formation from the imidazole compound and the epoxy group. The second step is the etherification from the negative charge of the 1:1 adduct and another epoxy group, followed by chain-growth polymerization. The green numerals indicate the numbering of atoms in the imidazole ring.



states might be responsible for the reported chemiluminescence in all three systems. Lukac et al. synthesized polymeric diketones, i.e. structures that would be analogous to those of oxidized epoxy resins, and found a phosphorescence emission centered around 550 nm [27].

The emissive groups are changing during the curing reaction, or at least the environment around them. However, determining the specific radiative pathway and studying the changing environment is complicated owing to the complex composition of this resin. At the beginning of the curing reaction, the chemiluminescence spectrum is the sum of the oxidation spectra of the base resin and the catalyst. This means that, at least in the liquid state, there is no energy transfer between the two compounds and that the emitting species of the catalyst are not “disturbed” when immersed in the liquid resin. The oxidation products of both are able to emit chemiluminescence from a priori excited ketone groups without any influence of neighboring chemicals. After curing, chemiluminescence becomes redshifted. In this system, several chemical reactions are to be considered: 1:1 adduct formation, epoxy homopolymerization, and epoxy-lactone reaction. Only 1:1 adduct formation and the epoxy-lactone reaction involve a change in the near environment of the catalyst compounds. CL emission would then arise following oxidation of these molecular groups or by energy transfer to these groups. Notably, imidazole derivatives are known to be very efficient light emitters when incorporated in polymer films [28,29] and when associated with aromatic groups [30]. This group represents one of the candidates for hosting energy transfer in a changing environment.

### *C. The relation between CL and curing conversion*

From the experimental observations, it can be inferred that the CL intensity profile and the spectral distribution of chemiluminescence can be used to follow the extent of the curing reaction, and several steps can be identified:

Firstly, in domains I and II, the CL intensity increases to a plateau that lasts for roughly 15 min. This is consistent with experimental evidence obtained with FTIR of an induction period of 5 to 20 min observed in the epoxy homopolymerization catalyzed with imidazole compounds [16,19]. In this period, the curing reaction is happening at a slow rate since 1:1 adduct concentration is not high enough to catalyze a large number of reactions. It is then likely that in this domain, crosslinking did not occur to a significant extent. This is supported by the shape of spectra 1 and 2 which are basically the sum of the oxidation spectra of the base resin and the catalyst, thus showing that only the oxidation of the two compounds is being monitored.

Secondly, in domain III (spectra 3 to 6), chemiluminescence changes drastically from that of domain II. Its intensity increases by more than an order of magnitude and the peak wavelength  $\lambda_{\text{max}}$  also increases. The spectral distribution differs significantly from those of the base resin and the catalyst alone. This strong intensity and this redshift is clearly the sign that an intense crosslinking reaction is occurring. It is also noticeable that  $\lambda_{\text{max}}$  increases at a much higher rate than the CL intensity, which means that only a very low amount of excited crosslinked species are sufficient to be detected using this method since they completely dominate the CL spectrum.

Finally, in spectra 7 to 9, which correspond to domains IV and V using the PM,  $\lambda_{\text{max}}$  decreases to stabilize at about 550 nm, which is the value observed with the cured resin. The PM intensity also drops by almost two orders of magnitude. In this regime, the crosslinking reaction would slow down significantly and be almost over after about 100 min.

#### *D. Contribution from the exothermicity of the reaction*

A deeper understanding of the mechanism behind the increase in chemiluminescence intensity during the curing reaction is still lacking. Some studies have shown, using FTIR and calorimetric experiments, that the chemiluminescence was related to the extent of the curing reaction of epoxy-diamine systems and the maximum of chemiluminescence also showed good correlation with gel times determined in rheology experiments [11,12]. For our system, the gel time was measured at about 53 min. The curing CL then seems to be correlated to the curing reaction and hence to the network formation. However, in our case, CL is caused by exoenergetic chemical reactions with ambient oxygen. It is not obvious why the curing reaction would increase the oxidation rate or why the oxidation byproducts would change during the reaction, as evidenced with the non-monotonous behavior of  $\lambda_{\max}$ ; and this mechanism is not clearly explained in the literature. In [11], the curing reaction of a glycidyl amine resin, tetraglycidyl 4,4-diaminodiphenyl methane (TGDDM), and an amine curing agent, 4,4'-diaminodiphenylsulfone (DDS), was investigated. The authors reported a monotonous decrease of the CL intensity during the curing reaction and a change in the activation energy was observed close to the gel point. This was attributed to a change in the physical state of the resin which limited oxygen diffusion past the gelation point due to increased viscosity. In [12], the curing reactions of three different base resins, two glycidyl ether resins – analogous to BADGE – and one glycidyl amine resin – analogous to TGDDM with the amine curing agent DDS were studied. A different behavior from the one observed in [11] was reported, even though similar chemistries were investigated. All three of these systems showed a behavior similar to the one reported in this study, with a chemiluminescence going through a maximum during the curing reaction. The CL maxima were close to gel times measured in rheology. Changes in quantum yield, viscosity, oxygen diffusion and resin color were advanced to account for the observed phenomenon. It should be noted that both studies used small amounts of resin, around 30-40 mg, placed in DSC pans. In our case, using larger samples of roughly 3 g was necessary in order to have enough signal to acquire spectra during the curing reaction within 5 min. Another hypothesis which was not reported could explain the increase in chemiluminescence during the curing reaction. Indeed, since it is a highly exothermic reaction, the temperature of the sample is expected to increase significantly, especially for bulk samples. Since CL is a thermally activated process that follows an Arrhenius law (with an activation energy of 35 kJ/mol [4]), an increase in intensity is expected.

To answer this question, DSC isothermal curing was realized at 90 °C and 100 °C and compared to the curing CL profiles of large samples of 3 g and smaller samples of approximately 30 mg placed in small aluminum pans (Fig. 10 a). It is clear that the overall shape of the DSC curves matches well that of the CL profiles. However, larger samples show a maximum of CL after 40 and 21 min at respectively 90 and 100 °C which is significantly earlier than the maximum heat flows observed in DSC at 56 and 28 min. When studying the curing of smaller samples, the CL peak is shifted towards longer times and the CL intensity show maxima at respectively 54 and 31 min which correlates almost perfectly with the exothermic peaks in DSC. The DSC curves were acquired for isothermal curing reactions at 90 and 100 °C, which should not necessarily be the case for CL experiments. Moreover, the reactivity of this resin greatly changes with temperature. For instance, at 100 °C the maximum of heat flow was measured at 28 min, an 18 min change compared to 90 °C, whereas at 75 °C only 20 % of conversion were measured after 2 hours of curing. A rise in temperature of several °C is expected during the curing reaction and could significantly change the reactivity of the resin, thereby accelerating the curing reaction. This phenomenon should be particularly present with larger samples, whereas smaller samples are expected to show a lesser increase in temperature. This

could explain why the maximum of CL of relatively large samples (3 g) does not correlate well with the gel time and the maximum of heat flow in isothermal curing, whereas it almost perfectly does for smaller samples.

To confirm this, a type K thermocouple was immersed in the resin during the curing reaction of a large sample at 90 °C. The temperature clearly shows a maximum between 37 and 40 min, with a maximum increase in temperature of 5 °C (Fig. 10 b). This strengthens the hypothesis of CL caused by exothermic events. It is also apparent from the CL curves at 90 °C (Fig. 10 a) that both the bulk and the small samples share the same overall CL evolution over the course of the curing reaction. The CL of the bulk sample (red curve) starts to deviate from the other one (blue curve) after approximately 30 min where the increase in temperature starts being noticeable.

The fact that the spectral distribution changes and that  $\lambda_{\max}$  exhibits a non-monotonous behavior clearly shows that the emissive groups are changing during the curing reaction. It could be indicative of intermediate network configuration and chemical composition. Several complex chemical reactions are simultaneous in this system and 1:1 adduct concentration, lactone concentration, network packing and physical state of the resin might influence the spectral distribution. The imidazole compound and the 1:1 adduct can both be regenerated during the curing reaction, which would again change the chemical composition of the polymer network. However, it is possible that another phenomenon would be taking place to explain the wavelength shift during the curing reaction. Indeed, the CL spectral distribution of the cured resin was measured at different temperatures from 100 to 175 °C (Fig. 10 b).

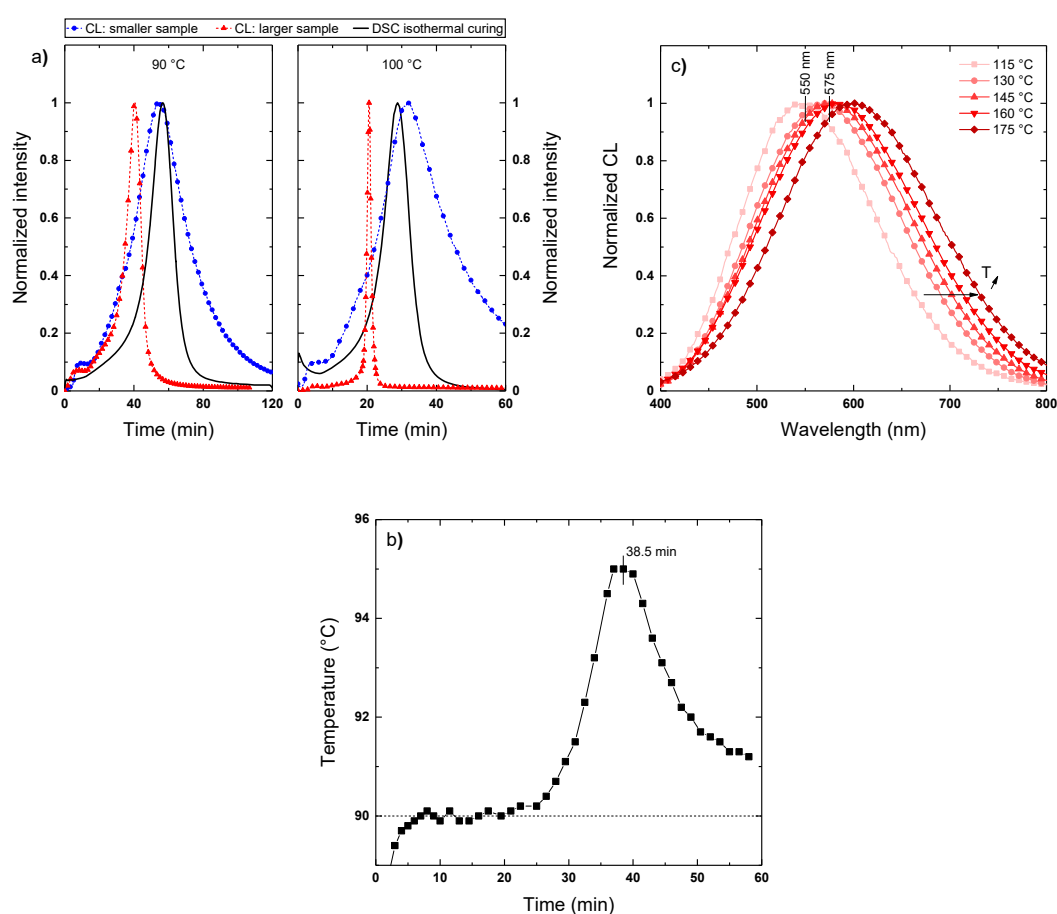


Fig. 10. a) Chemiluminescence during the curing reaction of small (30 mg) and large (3g) samples compared to heat flow isothermal DSC curing curves. b) Temperature in the resin during the curing reaction measured by a thermocouple immersed in the resin. c) CL spectral distribution of the cured resin at different temperatures.

The spectral distribution shifts to longer wavelength the higher the temperature. This behavior may be analogous to that of polypropylene (PP) in an oxidative atmosphere. New CL bands in the red region were seen to arise when PP was heated for long times at high temperature ( $> 150\text{ }^{\circ}\text{C}$ ) [7]. This was attributed to the formation of conjugated oxidized species. It is interesting to note that the CL spectral distribution becomes redshifted for temperatures higher than the  $T_g$  where a significant increase in oxygen diffusion is expected. For instance,  $\lambda_{\text{max}} = 575\text{ nm}$  at the CL maximum corresponds to a spectral distribution obtained at  $145\text{ }^{\circ}\text{C}$ , which is almost identical to the spectral distribution of spectrum 6 of the resin during curing. The fact that the spectral distributions match does not necessarily mean that temperatures are equal in both cases, but rather that the emitting species might be the same. Therefore, in the epoxy resin during curing, monitoring the CL spectral distribution would then give information on the nature of the oxidation by-products that are formed. More conjugated species might be formed when the reaction rate and the resin temperature are at their highest point (around 40 min).

## V. CONCLUSION

The chemiluminescence of an epoxy resin has been investigated by studying the cured resin, its two components separately and their curing reaction. An intense luminescence is observed only in air, which shows that chemiluminescence arises from oxidative chemical reactions. It is found that the chemiluminescence spectral distribution of the cured resin differs from both of the uncured resin or the catalyst alone. The new spectral distribution is attributed to the emissive species of the catalyst in a changed environment caused by the curing reaction. The CL is likely due to the imidazole compound present in the catalyst.

The chemiluminescence during reaction is believed to be representative of the curing reaction rate. This is supported by the correlation between the gel point, measured in rheological tests, isothermal DSC runs, and the maximum of chemiluminescence of small 30 mg samples. The increase in the chemiluminescence intensity during curing is believed to be caused partly by the exothermicity of the curing reaction, which increases the temperature and therefore the oxidation rate (visible as chemiluminescence).

The spectral distribution of the chemiluminescence changes over curing time, and  $\lambda_{\text{max}}$  shows a non-monotonous evolution. This might be due to intermediate chemical composition of network configuration of the material but the precise identification of this phenomenon is not straightforward since the catalysis of epoxy homopolymerization by imidazole compounds is not simple. It is also shown that a temperature effect is probably to take into account to explain this phenomenon, and the redshift of the spectral distribution observed for the cured resin at high temperatures might be useful to understand the nature of the oxidation by-products formed during the course of the curing reaction.

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