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Electroluminescence and thermo stimulated luminescence in an epoxy resin under uniform ac field

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Abstract: The critical field beyond which irreversible evolution of a material occurs and how this limit varies with temperature is of prime importance from the insulation designer's standpoint. The present work concerns electroluminescence (EL) measurements for an epoxy resin under uniform 50Hz ac field. We have studied the EL dependency on both temperature (20 to 72°C) and electric field (0 to 16kV/mm) under AC stress. The material investigated does not contain mineral fillers, and has a glass transition temperature of 65°C. We have observed two regions in the EL-field characteristics: a low field regime in which the EL threshold appears limited by the sensitivity of the detection set-up, and a higher field regime, above a threshold in the range 8 to 14kV/mm, with a higher slope in the characteristics. We have also observed a strong spontaneous light emission in the absence of applied voltage. The origin and consequences of this on EL are discussed.

INTRODUCTION

The background on the electrical behaviour of epoxy resins under non destructive electric field is tenuous, though these materials are extensively used as insulation. Of prime importance for the designer standpoint is the critical field beyond which field-induced irreversible evolution of the material occurs, and how this critical field varies with temperature.

Electroluminescence (EL) detection means that molecular excited states, by nature reactive, are created under field and thus the field threshold for EL detection might be related to the critical field defined above [1].

We have considered the EL dependence on both temperature (20 to 72°C) and electric field (0 to 16kV/mm). The range of parameters was chosen regarding the industrial applications of this epoxy resin, such as high voltage and low voltage transformers.

The investigated materials have the peculiarity to emit spontaneous light when they are heated above c.a. 40°C. Part of this work addresses this feature which of importance for EL interpretation.

MATERIALS AND MEASUREMENTS SETUP

Samples

Chemical data The investigated resin does not contain mineral fillers. It is produced by mixing an equal weight of hardener HY227 and resin CY225, thereafter referred to as base resin, and a small quantity of catalyser DY062, all components being Humtsman's (ex Ciba Geigy) references. The known chemical properties of the components are given in Fig. 1, where DGEBA means Diglycidyl ether of bisphenol A and MTHPA means Methyltetrahydrophthalic anhydride. The epoxy resin, obtained after 16h of curing at 100°C, has a glass transition temperature (Tg) of 65°C.

Macroscopic data All studied samples were obtained with the same mould, providing disks of 500µm (+/- 10µm) thickness and 110mm diameter. Most of the experiments were performed on metallized samples. Semitransparent electrodes, 300Å in thickness and 25mm in radius were deposited by gold sputtering.

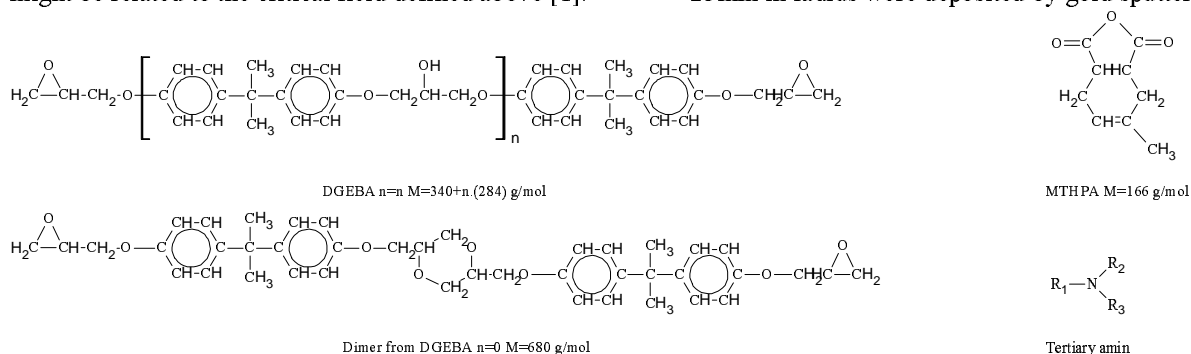


Figure 1: Known chemical formulation of components of the resin. The base resin (CY225) is constituted mainly by DGEBA with n=0 and 2 and a dimer. 50% hardener (HY227) is MTHPA. The amine is used in the catalyser (DY062).

Luminescence setup

Environment The same chamber, with main components depicted in Fig. 2, was used for EL and spontaneous (thermo-stimulated) light emission measurement. The lower electrode on which the samples rest is thermally controlled by a reservoir with thermostated liquid flow. Prior to measurements, the chamber is evacuated for 12 hours under secondary vacuum (10^{-6} mb), then an overpressure of nitrogen (1.2 bars) is introduced. The reason for using a nitrogen atmosphere is that thermal regulation is difficult to achieve under vacuum. Vacuum is normally used when making EL measurements at room temperature, to avoid any discharge phenomena. Nitrogen was chosen rather than air because oxygen may quench luminescence phenomena whereas nitrogen is more neutral. In these conditions, reasonable temperature control and homogeneity within the sample is obtained - even so there may be some temperature gradient in the system - and electrical measurements can be performed by reducing flashover risk. EL measurements were made at 7 temperatures between 20 and 72°C.

Electrical stressing EL measurements were realized under 50Hz AC stress. The automatic protocol of stressing consists in rising voltage by 0.5kV steps from 0 up to 8kV (r.m.s. values), with 120s rest time at each step, the ramp speed between steps being 300V/s.

Luminescence measurements A cooled Photo Multiplier (PM) is used to integrate the number of detectable photon each second, with a mean noise level of 0.87 Count per second (Cps) and a Standard deviation (Std) of 0.47 Cps. The top electrode has a ring shape in order to allow detection of emitted light. A mask is placed over the top electrode in order to detect only light emitted from the central part of the ring. An IR filter (cutting above 600 nm) is used to get rid of luminous emission artefacts due to an AC stimulation of gold [2].

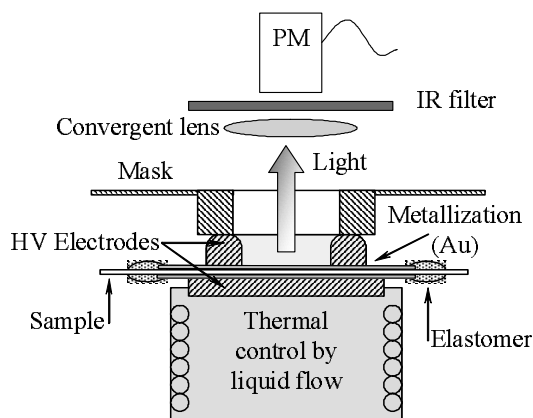


Figure 2: Electro-thermo luminescence measurement setup.

RESULTS AND DISCUSSIONS

Luminescence by thermo stimulation

Typical thermo stimulated luminescence Epoxy resin can emit light during curing [3]. In addition, it is referenced that long-lived luminescence can be produced spontaneously by thermo stimulation on a previously cured epoxy resin [4]. This behaviour is of importance for EL measurements performed above room temperature, since we then have to deal with two possible sources of light. Fig. 3 shows the luminescence measured in nitrogen atmosphere - on a previously cured sample - by rising the temperature to 72°C and keeping it constant. The maximum of light is obtained at the time temperature reaches 72°C; the signal decreases slowly afterwards. The decrease of the light appears exponential for about 30 min, and becomes slower afterwards. Luminescence has practically vanished after 4h at 72°C.

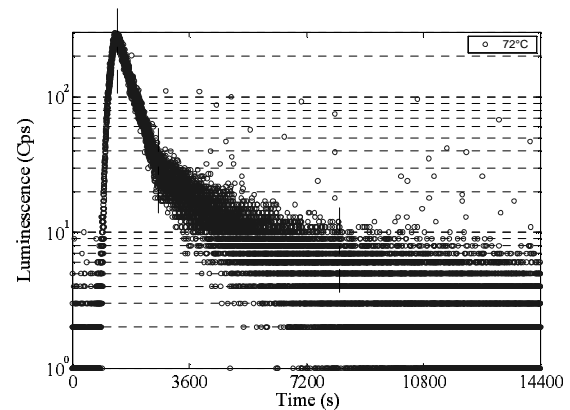


Figure 3: Typical luminescence measured at 72°C on a gold metallized epoxy resin through IR filter and under nitrogen atmosphere.

What is the origin of this phenomenon? The aim of the next section is to address this question by changing the nature of the atmosphere.

Influence of the atmosphere We have performed a series of experiments on a single sample free from metallization and without IR filter. The experiment consisted in:

- 1/ repeating the same experiment as above, at 72°C in nitrogen, and waiting for the emitted light to reach the photomultiplier noise level;
- 2/ cool to room temperature, wait for 48h, and repeat the experiment in the same conditions as in 1/
- 3/ cool to room temperature, expose the sample to air, wait for 48h, and repeat again the experiment.

Results obtained for cycles 1/ and 3/ are shown in Fig. 4. No light was detected in step 2/. The light level (cycles 1/ and 3/) was larger as compared to results of Fig. 3, primarily because the analyzed sample area was larger and also because there was no gold electrode and thus no related light absorption. Clearly, the nature of

the atmosphere has a strong effect on the light being detected. In step 1/, i.e. in nitrogen, luminescence is continuously decreasing (except for the time interval where the temperature is increased). In step 3/ a quasi steady-state level of light is measured.

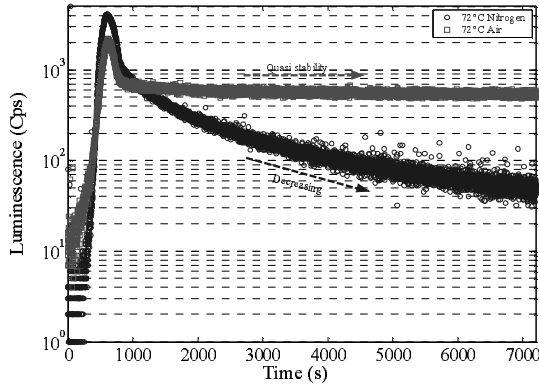


Figure 4: Spontaneous luminescence in nitrogen compared to air atmosphere, measured in the same non-metallized sample. The experiment in air was performed after that in nitrogen.

At short time, the dynamics seems to be similar between the one in nitrogen and the one in air, but after this stage the behaviour is quite different. Actually, the air seems to constitute an infinite reservoir for the luminescence of our epoxy resin, whereas luminescence in nitrogen could be decreasing due to consumption of oxygen or water adsorbed in the material. The dynamic observed at short time (peak in luminescence, similar for the 2 materials), is not related to an overshoot in sample temperature since heating is provided by a thermostated liquid.

The mechanism behind this process is not understood. A post-curing effect, i.e. chemiluminescence following uncompleted curing was envisaged. This has been discarded for two reasons: first, it is observed at relatively low temperature (from about 40°C and on, cf. next section) whereas samples have been kept at 100°C for 16h during curing; second one would not expect a strong influence of the atmosphere if such a process holds. Oxidation - of hydroxyl and epoxy group [5]- could be a phenomenon contributing to the luminescence, but it seems to be an unsatisfactory answer to explain all of observation. A similar result was observed by Suzuki & al. [4] on an epoxy resin of different nature. They investigated in detail the amount of light detected as a function of the time the sample was kept at room temperature, from which they deduced that regeneration of light could be controlled by diffusion of oxygen within the material.

Whatever the mechanism at the origin of this emission, it constitutes an important parameter to take into account since luminescence being measured under field

at elevated temperature will be partly due to this process, which is time dependent with a slow kinetics.

Luminescence under electrical and thermal stimulation

EL-field characteristics versus temperature Fig. 5 shows the EL vs. field characteristics obtained at different temperatures. Experiments were realized consecutively on the sample, starting from room temperature. The sample was not previously heated. At the end of each voltage cycle, we waited for 6 min with the field off, and then the temperature set point was increased up to the next step. The temperature was equilibrated for 10min prior to the next voltage cycle.

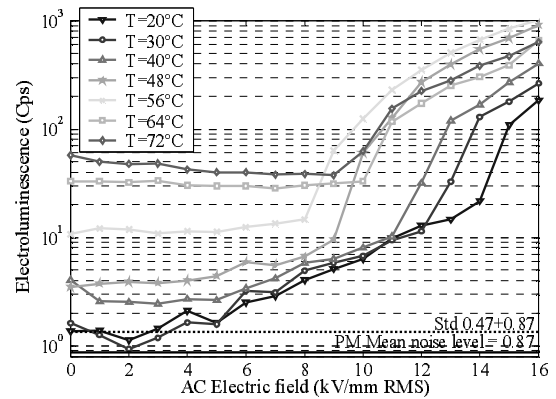


Figure 5: Electroluminescence vs. AC field characteristics measured consecutively from 20 up to 72°C on an epoxy resin under nitrogen atmosphere.

Four observations are worth pointing out: i/ the strong temperature dependency of the spontaneous luminescence can be visualized observing data at 0kV/mm; ii/ a first threshold of electro-luminescence can be seen between 2 and 4kV/mm at low temperature, (this might be related to the sensitivity of the detection system); iii/ a second threshold defining an increase in the EL-field slope, is observed between 8 and 14kV/mm, clearly depending on the temperature; iv/ above 56°C, the upper threshold is shifted to high fields whereas it was continuously decreasing up to that point.

The increase of the EL threshold for temperature >56°C, along with the decrease of signal being measured at high field, could be related to the fact that T_g of the investigated epoxy is in that temperature range. One could relate these observations to the decrease of luminescence yield, with temperature rising, by a reduced interaction between chains. The other possibility we have to consider is that this process may be related to the exhaustion of the spontaneous luminescence. Indeed, in the data presented in Fig. 5, the source of the spontaneous light emission is continuously consumed as cycles are cumulated, and this may have an influence on the luminescence contribution due to the electric field excitation. The next

section addresses this feature by means of two targeted experiments.

Influence of preconditioning The first experiment consisted in performing measurements directly at 64°C then at 72°C without applying the initial steps in temperature. Results are presented in Fig. 6. Light increases faster at low field than in the previous experiments, and also the signal at high field is higher. These results discard the possibility that the observed effects above 56°C in Fig. 5 be exclusively related to T_g of the epoxy. At the same time, it stresses the influence of thermal conditioning on the EL signal.

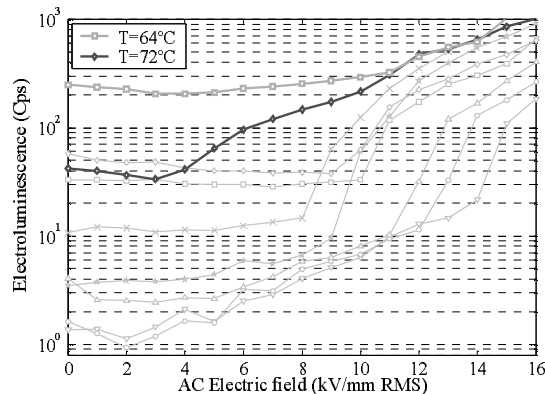


Figure 6: EL measurements repeated consecutively at 64 and 72°C on an epoxy resin under nitrogen, superposed to data of Fig. 5.

The second experiment (Fig. 7) was carried on a sample previously annealed at 72°C for a time long enough to make the spontaneous luminescence disappear under nitrogen. In that case, the first voltage cycle was applied at 72°C and the temperature was decreased for the second one. Experiments could not be achieved below 56°C due to residual stresses inducing mechanical deformation of the sample when crossing T_g under temperature gradient.

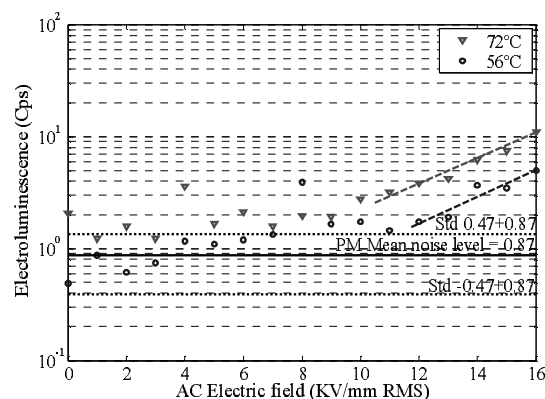


Figure 7: Electroluminescence repeated consecutively at 72 and 56°C on an epoxy resin under nitrogen and after exhaustion of luminescence by thermo stimulation.

Due to the much lower signal levels, it is difficult to observe the same trends in the characteristic as previously - with two regimes of emission - except the upper threshold which is detectable in the range 10-12 kV/mm. The level of light is much lower than previously. Hence, the phenomenological result from this study is that the level of EL - i.e. the contribution to signal corresponding to excitation by the electric field - decreases when we are in conditions of low spontaneous emission. The highly hypothetical explanation to this behaviour is that species (if any) formed during sample storage in the ambient are those excited under field. A step forward in the understanding of these phenomena would consist in recording emission spectra of the two kinds of emission. Though the level of light is relatively weak, this will be attempted in the near future.

CONCLUSIONS

The main outputs of this work are as follows: (1) spontaneous luminescence due to thermo stimulation disappears (in the limit of the sensitivity of the set-up) within 4h at 72°C in nitrogen atmosphere; (2) spontaneous luminescence can be regenerated by sample exposure to air at room temperature. (3) air seems to provide an infinite reservoir for this luminescence phenomenon; (4) EL exhibits two levels of field threshold, the first level being sensitivity-limited and the second appearing in the range 8 to 14 kV/mm, depending on temperature and on material preconditioning; (5) the upper EL threshold decreases when the temperature is increased, considering conditions of equivalent preconditioning; (6) The EL level decreases strongly after thermal preconditioning, and this appears to be correlated to a decrease of the spontaneous emission.

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