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Monitoring electrically-active defects in silicafilled epoxy using light detection

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Abstract- Epoxy resins have been used for long as the insulation of electrical systems. It is generally formulated with a dispersion of micro-fillers to improve thermal and mechanical properties. However, there are concerns on the possible influence of these fillers on the electric behavior, especially on the long term ageing under functional stresses. Defects (decohesion between matrix and fillers, macro and micro-voids in the resin, etc.) can be detected using tomography but there is no indication of the harmfulness of these defects under electrical stress. The possibility of monitoring defects by electroluminescence is put forward in this work.

I. INTRODUCTION

The use of silica to reinforce polymeric insulations like epoxy resin is used in industries essentially for its dielectric along with thermal properties since the adjunction of silica improves the thermal dissipation.

Such materials may undergo ageing under thermo-electrical stresses, and interfaces between the filler and the matrix may constitute weak points with the formation of voids and delamination, particularly as the temperature is cycled. The objective in this work is to determine if interfaces can be damaged under electrical stress and if electroluminescence (EL) can be used as optical diagnosis.

Usually, EL is defined as light emitted by molecules excited by an electric field. It refers to the light produced by the material itself through interaction of electron of high kinetic energy with the molecules, producing excited states or through recombination of electron-hole pairs. If voids or delaminated areas are present in the material, light is expected to be emitted also by the gas occupying such defects even though microdischarges cannot be detected by conventional means. The search for a sensitive tool is of particular relevance here as experiments are carried out at low field with r.m.s. values typically up to 9kV/mm. This is a challenging aspect as, even though optical techniques are well known for their sensitivity, to our knowledge electroluminescence spectra at such low field values have never been reported in the literature. The devices used for detecting such low signal are presented in the next section along with materials under study.

II. EXPERIMENTAL

A. Material – Samples

The material under study is a silica-filled epoxy resin; with 60% by weight of silica. The matrix is made of equal parts of resin (Diglycidyl ether of bisphenol A) and of a phtalic anhydride as hardener, and of a small amount of tertiary amine as catalyzer [1]. The silica particules size is widely dispersed, their diameter ranging from 1 to 100µm.

The samples have been molded into disks of 1 mm ($\pm 20\mu$ m) thickness and a diameter of 110mm and cured at 100°C for 16h. For the needs of EL experiment, semitransparent gold electrodes, 50mm in diameter, have been deposited by sputtering. The thickness of the upper electrode, put to the HV and through which light is detected, is of 30nm. For the lower electrode, a larger thickness was used, 60nm, to improve the electrical contact with the ground electrode.

A silicone rubber ring was laid at the periphery of the electrodes in order to avoid emission in regions of uncontrolled field. Fig. 1, shows a schema of the sample once conditioned.

B. Experiment environment

A light-tight chamber is used to carry out experiments. It is equipped with pumping units allowing to make experiments under secondary vacuum. Most often, EL experiments are carried out in vacuum to avoid any gaseous discharges in the environment of the sample. If some signal is related to microdischarges in the sample, then its features should be sensitive to the ambient atmosphere. For these reasons, in the present experiments, we have carried out measurements under vacuum (typically 2 to $4x10^{-6}$ mb), in air, and under nitrogen atmosphere at 1200 mb (since the oxygen present in air could quench part of the luminescence being detected).

Two brass electrodes are used to make measurements: the lower one is a massive electrode connected to the ground. The upper one is put to the HV; it has a ring shape to allow light detection, cf. Fig. 2. Finally, a mask is put on the ensemble to



Fig. 1. Sample for EL measurement

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detect only light coming from the central part of the ring electrode.

Three kinds of measurements are carried, that are integral light detection by photon counting, spectra analyses of the emitted light and imaging of the emission in the sample plane.

The integral light detection is made using a photomultiplier (model R943-02 from Hamamatsu) working at -30°C. The spectral detection range is 180 to 900 nm. A dwelling time of two seconds is used for monitoring the emitted light. The average noise level is 1.49 counts per 2 seconds with a standard deviation of 1.02 counts per 2 seconds.

The image of the emission in the sample plane has been carried out using a cooled (-130°C) charge coupled device -CCD- camera (model spectrum one D-91 from Jobin-Yvon). The CCD is made of 512 x 2048 pixels of size 13.5x13.5 μ m². The principal advantage of this device is the possibility of using long exposure times (several hours) without perturbation due to the noise level. The CCD is sensitive in the wavelength range 200-1000nm.

Finally, spectral analyses of the light are made with the same CCD, introducing in front of it a grating monochromator. With the grating used (groove density of 133 per mm), the region 285-1000nm is resolved into about 1800 points. As shown in Fig. 2, a mirror installed on a translational guide allows deviating light towards the CCD when such experiments are carried out.

All experiments have been realized under 50Hz AC stress; all field values reported herein refer to r.m.s. values. For recording EL-voltage characteristics, the voltage was increased from 0 to 9kV in steps of 1 kV lasting for 5 min. The voltage is raised at a rate of 300V/s between steps. For acquiring spectra or images, as the integration time can be very long, the voltage is set manually to a given stress.



Fig. 2. Arrangement of the experimental set-up

III. RESULTS AND DISCUSSION

A. EL-field characteristics

Fig. 3, shows a typical measurement of light during increase of the voltage by 1kV steps. Each point represents a number of photons collected during 2 seconds (and converted in a number of pulses – or counts – by the signal conditioning channel). The signal is relatively stable at each voltage level. In what follows, averaged values of the signal at each voltage step will be presented.

Through a systematic analysis of the emission for a population of samples, being filled or not, we have evaluated the impact of the atmosphere on the shape of the EL-field characteristic and on the EL level. Fig. 4, shows an example of results obtained for the same sample, in air, nitrogen and vacuum $(2.5 \times 10^{-6} \text{ mb})$. Some differences in the level of light being detected could be observed, depending on the atmosphere; however, there was no systematic trend on the effect of such or such atmosphere when characteristics were smooth. In the example the signal is lower for air and higher for nitrogen. In fact, differences could be observed only when instabilities appear on the characteristics.

A second aspect which was treated is the statistic variation in the form of the characteristic with samples of different roughness (due to different mould being used) and with either silica-filled samples or pure epoxy samples. Fig. 5, shows a panel of characteristics obtained for various samples and atmosphere. The signal being measured span over large



Fig. 3. Example of EL rough data recorded in air. The voltage was increased in steps of 1 kV lasting for 5min, and the PM signal was recorded continuously with a dwelling time of 2s.



Fig. 4. EL-field characteristics of an unfilled epoxy in different atmosphere.

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Fig. 5. Superposition of EL-field characteristics for various samples and with either air, vacuum or nitrogen as atmosphere. Solid symbols: silica-filled materials; open symbols: un-filled samples.

intervals: roughly a sample-to-sample variation of x40 can be obtained at the extreme. It can also be observed that the variation factor is larger for high field than for lower ones.

Looking in details at these characteristics, it has been observed that some instabilities appear during the increase of the voltage, in the form of a step in the signal above a voltage ranging from 4 to 8kV, depending on samples. Such steps are responsible for the strong signal observed in some samples (>1000c/2s at 8kV/mm).

The criterion on the apparition of instabilities has been used to classify samples into two groups having different typologies of EL-field characteristics. The typology 1 corresponds to light emission which begins to appear at 1-2 kV and increases regularly with the field, being stable at each voltage level. This concerns most of silica-free samples: over 80% of them are of type 1 (under 1000c/2s). For typology 2, a steep increase at a given voltage level occurs and the emission becomes unstable under constant voltage. This concerns a majority (60%) of silica-filled samples.

B. EL spectra

Several wavelength-resolved spectra have been recorded at different voltages and with different samples. Due to the low signal being measured, the time necessary to get an exploitable signal could be long (of the order of 1 hour). Also, for the same reasons, spectra could be recorded only in the high field range of the characteristics. We have observed that different spectra are obtained depending on the typology of the characteristic of the sample under test. To characteristics of typology 1 correspond broad non-structured spectra in the red domain, Fig. 6.a (the spectrum peaks at about 780nm). In case of typology 2, the emission appears in the same wavelength range; however clear structures appear in the spectrum, cf. Fig. 6.b.

Emission in the red domain has already been reported when investigating EL of insulating polymers. As it is difficult to envisage chemical groups having emissions in that range, this red emission has been interpreted as surface plasmons –SPrelaxation [2]. A plasmon is a collective oscillation of electrons in a metal. If these oscillations can couple to surface roughness, they can radiate light. SP spectra reported in the literature for MIM junctions are usually broad. Structured spectra have been reported in the case of SP excited by electrons tunneling



(a) Sample of typology 1. Integration time = 30 min; Voltage = 9 kV



(b) Sample of typology 2; Integration time = 30 min; Voltage = 7 kV

Fig. 6. Examples of EL spectra obtained on samples having characteristics of different typology.

between a scanning tunneling microscope –STM- tip and a sample [3]; however, the structure has been explained by geometrical factors in the arrangement.

It is not clear yet as to why samples exhibiting instabilities in their EL-field characteristic do lead to these specific structures in the EL spectrum. Are the conditions of excitation of SP in STM gathered here? Are there other mechanisms of emission like gaseous discharges? The point is that there are no tabulated emission bands for gases in this wavelength range.

Finally, we have not identified specific signal linked to the epoxy itself, presumably because the red (SP) emission overlaps it.

C. Imaging of the EL in the sample plane

Images of the emission in the sample plane have been recorded with the CCD as described before and an example of such image is shown on Fig. 7.a. Homogeneous emission has been observed irrespective of the typology of the corresponding EL-field characteristic. The homogeneous aspect of the image is apparently not related to the long integration time used here since in case of porous materials in which discharges are known to appear, bright spots could be observed even for long integration time, see Fig. 7.b. The result of these images have shown homogenous signal in the two types of spectra. The promising aspect here is that a region of enhanced emission is clearly visible in Fig. 7.a), a feature which was not observed in un-filled materials and that could be related to the defects advocated above.

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(a) Filled epoxy. Voltage = 9 kV; integration time = 2 h. The circle indicates a region of enhanced emission.



(b) Porous 150 μ m-thick porous polypropylene sample. Voltage =3 kV; Integration time = 0.5h.

Fig. 7. Images of the EL emission in the sample plane. The size of the images is $27.6 \times 6.7 \text{ mm}^2$.

D. Routes for discarding SP emission

One way to discard light related to SP emission consists in inserting an optical filter that cuts emission at wavelengths above 600nm. Fig. 8 compares the characteristics obtained with and without filter. The fact that the field dependence of the 2 characteristics are not proportional implies that the spectrum is field-dependent and hence that possibly several emission processes contribute to the emission. As regards potential emissions in pure epoxy, it has been shown that the longer wavelength emission detected is related to oxidation of the hardener of the epoxy [4], which peaks at 580nm. Clearly, such emission would be in the short wavelength tail of the SP emission and the two processes are difficult to separate using a red-censoring filter. Nevertheless, the shape of the characteristic indicates that the relative amplitude of the emission under 600nm increases with the field.

The best solution to avoid SP emission consists in using an electrode material that radiates out of the wavelength range of interest, which is the case of indium tin oxide (ITO) since its SP emission is in the far-IR. Another advantage of ITO is its transparency in the visible range, which is not the case of gold; the drawback being that the deposition technique is somewhat more complex. Fig. 10 shows an example of characteristic obtained with 220 nm -thick ITO electrodes. The shape of the characteristic is approximately linear and conforms more to that obtained with red-sensoring the signal of gold-metallized samples. Most importantly, the spectrum obtained with ITO electrodes is clearly different from that obtained with gold, cf. Fig. 9. The peak is shifted to about 570nm, consistently with that obtained during thermal oxidation of the resin [4] and also with cathodoluminescence measurements (results not shown here), being strong supports that this emission is really characteristic of the material. Work is in progress to develop measurements with ITO electrodes.

IV. CONCLUSION

Two typologies have been identified in the EL spectrum of gold-metallized pure and silica-filled epoxies. The spectrum is always in the red domain, with either no structures or clearly identified structures. In the first instance, the EL-field characteristic are smooth, while in the second one, they exhibit



Fig. 8. Example of EL-field characteristics obtained with and without red filter on a filled sample.



Fig. 9. EL-field characteristic of a filled sample metallized with ITO.



Fig. 10. EL spectrum of a filled 11O-metallized samp Integration time = 30 min ; under 12 kV

a sharp increase in the signal at a given field level. As the later concerns in majority filled samples, the behavior could reflect the existence of voids at the epoxy-silica interface. The use of ITO instead of gold electrodes appears as a promising solution for avoiding SP-related EL, allowing so to isolate materialrelated emission.

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