Electroluminescence from silicone gel in needle-plane configuration

Kazeem ODESANYA[1], Gilbert TEYSSEDRE[1], Jean-Louis AUGE[1], Dongxin HE[2]

(1) Laplace, University of Toulouse and CNRS, Toulouse, France.
(2) School of Electrical Engineering, Shandong University, Jinan 250061, China.

ABSTRACT - This paper examines the behaviour of EL emissions in a silicone gel material. Due to the challenges in achieving homogeneous field configurations with soft materials, the study was conducted using a needle plane arrangement at various applied voltages up to 10 kV, and a constant frequency of 50 Hz. The voltage dependence of the EL intensity and of EL phase pattern reveal that certainly several mechanisms of light excitation are active. Given the very high field set near the needle tip, discharge as well as material degradation may be at play. Electroluminescence spectra were recorded and compared to photoluminescence and cathode-luminescence spectra. A strong emission band was observed at 590 nm under electron beam irradiation and attributed to material degradation. Also, a weak fluorescence emission was identified. As regards the EL spectrum, it was concluded that discharges are probably the main source of light. Extra work is necessary to exploit EL measurements in silicone gel.

Keywords—Electroluminescence (EL), Silicone gel, Divergent field, Phase resolution, Luminescence

1. INTRODUCTION

Electroluminescence involves the emission of light from an insulating or semiconducting material under the application of electrical stress. In the context of electrically insulating materials, electroluminescence (EL) is considered as an interesting technique to probe material degradation under pure electrical stress and to point on degradation processes. As electrical charges are necessarily involved in the EL excitation, either through impact on molecules by hot carriers or by bipolar charge recombination, it constitutes a way of exploring the interactions between charges and the material under stress [1]. Indeed, the question of the origin and action of charges appears as fundamental drivers for materials endurance. The accumulation of charges has been linked to some of the causes of ageing, degradation and failure of insulating materials. Indeed, charges can eventually lead to electrostatic discharges and breakdown as a result of the high electric fields created. A second harmful consequence of charges is their kinetic energy that can lead to molecular excitation and consequent chemical reactions. An ultimate consequence of material degradation is treeing phenomenon that leads to breakdown [2].

Electroluminescence has therefore been considered as an interesting technique to probe the early signs and occurrence of ageing, and the threshold field for light emission viewed as the threshold stress for material degradation [3][4]. Light emission may also be related to ionization of the gas either within the insulation or around it due to partial discharges (PD) or to the development of treeing phenomena.

Our purpose in this work is to initiate research on the EL in silicone gel, which is used in high demanding application as insulation in power modules. Silicone gel is used for encapsulation to prevent in situ electrical discharges in air and to protect substrates, semiconductors, and connections against humidity, dirt, and vibration [5]. The research faces difficulties linked to the very nature of silicone gel.

Indeed, in works achieved in the last decades, EL was observed on flat samples in homogeneous field configuration, with samples provided along-side semi-transparent electrodes in order to get stable response over large surface and to also control the electric field [4]. When dealing with soft or fluid materials, working with such arrangement is not easy as electrodes deposition needs to be achieved on both faces of the sample while precisely maintaining the gap between them. In this work, we are back to needle-plane configuration on silicone gel as in the pioneering works on EL in dielectrics [6]. In addition, there are few literature records related to luminescence from silicone gel except for studies on partial discharges and treeing [7], and some reports on the use of silicone elastomers as matrices hosting luminescent particles [8]. The present contribution therefore constitutes a first exploration of the feasibility of EL measurement in silicone gel, and more generally of its luminescence properties.

2. EXPERIMENTAL PROCEDURE

The material used in this study is Sylgard 527 silicone gel, which was crosslinked for 4 hours at 65°C after being placed under vacuum to remove air bubbles.

2.1. EL detection

The structure of the cell holding the transparent gel is shown in Fig. 1. It is composed of metallic plates separated by insulating glass spacers. A set of 5 needles are inserted through some holes in the plate to connect to HV. The reason for using
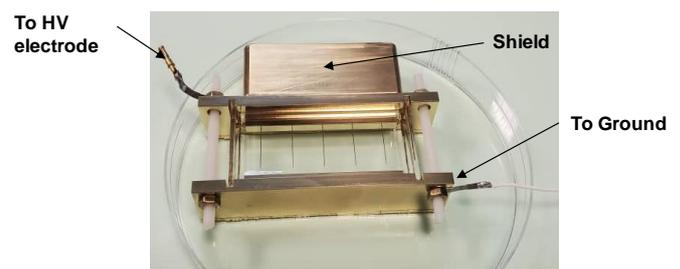

Fig. 1: Sample holder showing the needles embedded in silicone gel.

several needles is to increase the amount of generated light. The distance between the needle tips and the plate set to the ground is 2 mm. The needles' tip radius of curvature was estimated to 3.5 μm [9]. The distance between needles is 11 mm. A mask is put on top of the cell in order to isolate the light emitted in the tip region.

Experiments were performed in air in a light-tight chamber previously used for EL detection [4]. EL measurements were achieved under 50 Hz sine voltage. Integral light detection was achieved with a cooled photomultiplier (PM, R943-02 from Hamamatsu) working in photon counting mode. The 50 Hz ac voltage was applied using a 10 kV voltage amplifier from Trek associated with a function generator. EL-phase patterns were recorded by synchronizing PM pulses acquisition and phase of the ac stress. Two hundred (200) memory channels of the PM pulse counting board were used with a dwell time of 100 μs. Accumulation was made over 20 000 periods to get a total integration time of 2 s per memory channel. The voltage was increased in 500 V (all voltages are given as peak values) steps. The EL vs. voltage characteristics were obtained by averaging the PM counts obtained in the EL-phase patterns at each voltage.

2.2. Luminescence spectra

Some wavelength-resolved luminescence spectra were recorded when the level of emitted light was sufficient. The spectral analysis of the emitted light was performed using a grating dispersive system (Jobin Yvon CP200) coupled to a cooled CCD camera (Synapse from Jobin Yvon). Typically, EL spectra were recorded with an accumulation time of 5 min, using a 0.5 mm width slit for the dispersive system. In order to identify the nature of emitted light, and to attempt to differentiate light emitted from discharges from that produced by excitation of the material, complementary methods were used. At first, photoluminescence (PL) was achieved by excitation of the material with UV light in the range 220-300 nm using a 150 W xenon source coupled to a double-pass monochromator. Secondly, cathodoluminescence (CL), i.e. luminescence emitted under excitation by an electron beam was achieved in secondary vacuum with an energy of the beam of 6 keV, and a beam of current of about 60 μA. Cathodoluminescence has been reported as producing emission spectra similar to those found in EL, but with a far greater emission intensity [10]. For PL and CL experiments, silicone gel was prepared as previously and placed in an aluminium pan as a disk of about 5 cm diameter and 5 mm thickness. The same chamber and detectors as for EL were used.

3. RESULTS AND DISCUSSION

3.1. EL vs. voltage phase patterns

The detected signal exceeds the noise level of the PM for an applied voltage of 2 kV. The phase patterns appear well resolved beyond a voltage of 3 kV. Fig. 2 shows various patterns obtained with applied voltages in the range 3 to 10 kV. Generally, EL is detected in advance of the voltage peak, at least as far as homogeneous field experiments are concerned [4]. Here, we can see that as the voltage is increased, the signal tends to become in-phase with the applied voltage. This indicates that at least two mechanisms of light excitation could be at play. The emission stays symmetrical with regard to the polarity of the voltage. This is an expected behaviour when investigating EL with perfectly symmetrical electrodes arrangement on samples with negligible optical absorption of emitting light: considering that light is
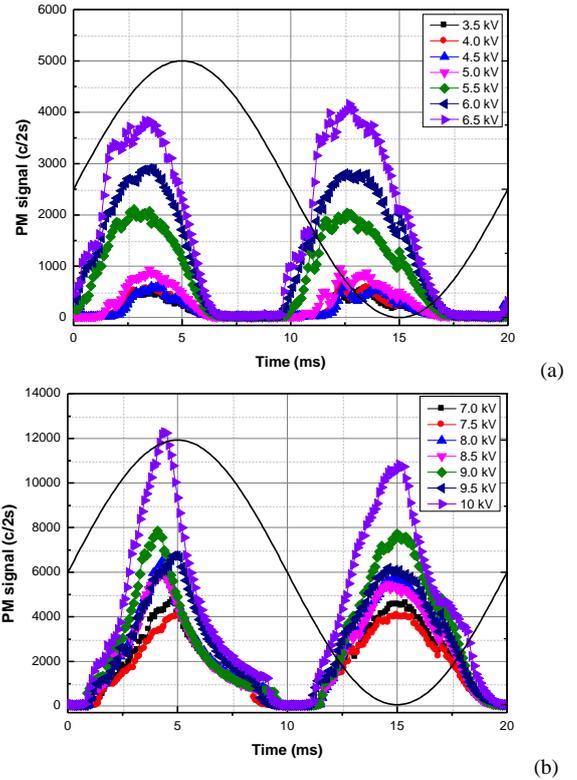

(a)

(b)

Fig. 2: The EL phase patterns for different crest voltages of the applied stress in the range (a) 3.5 – 6.5 kV, (b) 7 – 10 kV. Y-scale given in counts per 2 s.

generated upon charge injection at the electrodes, processes appearing in one half period at one electrode should be the same as those appearing at the opposite electrode in the second half-period. There is no reason for having identical charge injection process for positive and negative voltages. As in needle-plane configuration essentially only one electrode is active, the EL pattern should be non-symmetrical [11]. Note that light arising from EL and from PD activity was revealed in insulating liquids in divergent field configuration: both were highly non-symmetrical [12]. In general, it is considered, for solids, that discharges in advance in respect to the voltage arise from internal (voids) discharges while signal in phase reflects external discharges [13].

3.2. EL vs. voltage characteristic

The data used in Fig. 2 have been averaged in order to obtain EL vs. field characteristics and the result is given in Fig. 3. There are clear steps in the increase of the voltage, which confirms trends found for the phase pattern. It can be supposed that light
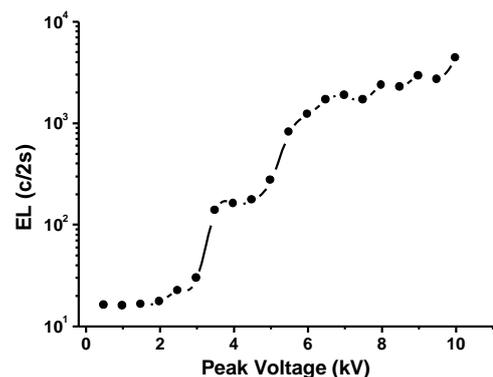

Fig. 3: EL vs voltage characteristics.

is triggered by different mechanisms in the different voltage ranges. There is however no obvious relation between the phase of the EL pattern, Fig. 2, and the steps in the EL intensity, Fig. 3. The EL becomes more in phase with the voltage at 7 kV while the last plateau in Fig. 3 is reached at 6 kV.

3.3. Electric Field Estimation

The main question to address here is on the origin of the light. Given the sample configuration, emission can be produced from the gel itself and/or from discharges occurring near the tip.

An important information is the field at play in these experiments under a strongly diverging field. The electric stress along the axis of the point-to-plane electrode system can be approximated by the following equation [14]:

$$E(z) = \frac{2V}{\ln(4a/r)} \frac{1}{2z + r - z^2/a} \tag{1}$$

where V is the applied voltage, z the distance from the needle tip, a the distance between needle and plane electrode, and r the radius of the needle tip. Fig. 4 shows the variation of the field with the distance from the tip along the axis. For an applied voltage of 10 kV, the field at the tip reaches 738 kV/mm which largely exceeds the breakdown field of 24 kV_{peak}/mm (17 kV_{rms}/mm) [15]. The field stays higher than 100 kV/mm over more than 20 µm from the tip: material excitation/ionization very likely occurs near the tip and possibly leads to voids formation and discharge. Note that if the light comes from PDs produced in voids, the EL should be in advance in respect to the voltage [13]. Treeing could follow. However, in the present sample arrangement, treeing would need much longer time/higher frequency to be formed according to published results [9].
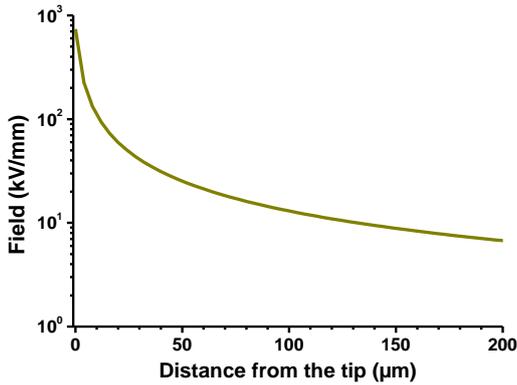
Fig. 4: Field variation along the tip axis for an applied voltage of 10 kV.

3.4. EL spectrum

Fig. 5a shows the EL spectra obtained under an ac voltage of 8 kV for an integration time of 5 min with the CCD camera. The signal is really weak, though reproducible considering 2 consecutive spectra. The maximum emission is at about 350 nm. Due to the weak intensity and the poor spectral resolution of the detection system, it is not possible to distinguish if the spectrum is characteristic of a gas discharge, with narrow bands or a solid with much broader bands. Emission due to discharge is usually expected in the range of 300 - 450 nm see below.

Fig. 6 shows an example of emission spectrum from partial discharges in air-solid interface [16]. The bands in the near-UV region (300 – 450 nm) are all characteristic of the N_2 molecules.

In that region, the reported spectrum is the same for a corona discharge in air (no dielectric) [16]. Very similar spectra are reported for corona discharge in air under DC or 50 Hz ac stress [17]. For spark discharges or arcs, the spectrum is richer in the range 400 - 600 nm [18]. Clearly, the recorded EL spectrum is not inconsistent with the one characteristic of PDs. For these reasons, we have considered analysing light from silicone gel using other excitation sources.

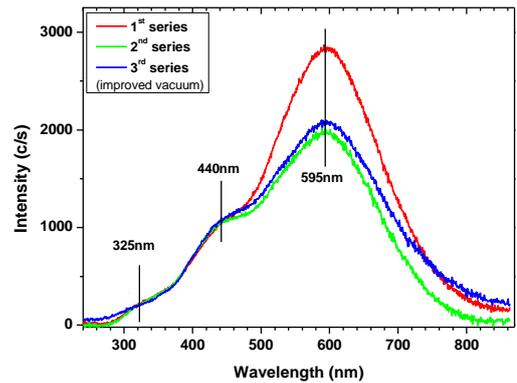### 3.5. Photo- and cathodo-luminescence spectra

Figures 5b and 5c show the emission spectra obtained by exciting with photons and with an electron beam, respectively. Photoluminescence is certainly the most common method to excite light. The photoluminescence intensity of silicone gel (Fig. 5b) is really weak compared to other polymers. The material (more precisely polydimethylsiloxane -PDMS-, which
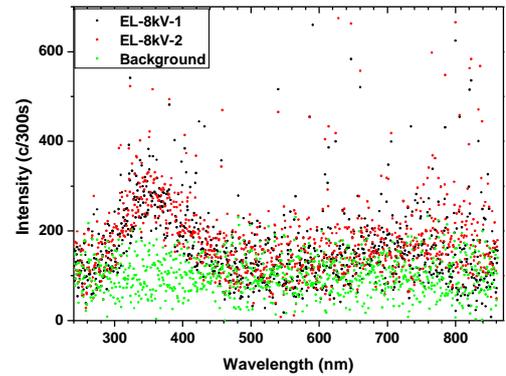
(a) Electroluminescence under 8 kV peak voltage
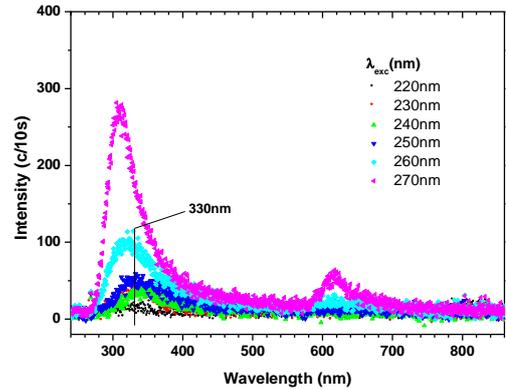
(b) Photoluminescence with excitation at wavelengths indicated in the caption

(c) Cathodoluminescence under 6 keV electron beam

Fig. 5: Luminescence spectra from silicone gel obtained using different excitation sources.
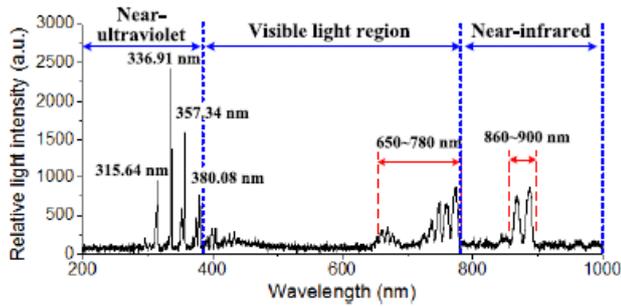
Fig. 6: Emission spectrum characteristic of partial discharges in insulation (paper-polyester composite film) -air system at a frequency of 5 kHz [16].

is the main constituent of silicone gel) does not absorb much above 300 nm [19], the reason why it is essentially transparent. The perceptible fluorescence from the material is at about 330 nm considering the result with an excitation wavelength of 250 nm. For longer excitation wavelength, the long wavelength tail of the excitation beam appears (an optical filter cutting under 300 nm is used in these experiments to remove the excitation beam). This feature explains the apparent blue shift of the emission when exciting at wavelength above 250 nm. The peak at about 600 nm is the second order of that at 300 nm and is due to the response of the grating monochromator.

Some details on the formulation of silicone gel, considered as a 2-components room temperature vulcanisable silicone (RTV), are available [20][21]. Polydimethylsiloxane – the main component of the gel (see structure in Fig. 7) – is essentially a non-luminescent material that can be used as matrix for hosting luminescent particles [8][22]. The only unsaturation appearing can be the vinyl group (–CH=CH$_2$) introduced for crosslinking, which in principle is non-luminescent. Though the literature confirms that PDMS is weakly- or non-luminescent, a previous report gives emissions in the range 300 - 350 nm with a maximum at about 340 nm [23].

Another way of exciting light is with e-beam irradiation. Previous works from our group showed that cathodo-luminescence spectra reproduce rather well those obtained in EL but with far greater intensity [24]. The obtained spectra for an energy of the beam of 6 keV are shown in Fig. 5c. Each of the spectra shown is the average of 10 spectra recorded consecutively with an integration time of 1 s each. The experiment was repeated to check if an evolution occurs upon irradiation. Three bands are clearly revealed in these spectra, with maxima at 325, 440 and 595 nm. There is no obvious evolution of the bands with the time of irradiation.

Spectra shown here are very similar to those reported by Torrisi et al. on irradiating PDMS with protons of 1.5 MeV energy [26]. One main broad peak was reported at 570 nm with a shoulder at around 450 nm. The region under 350 nm was not
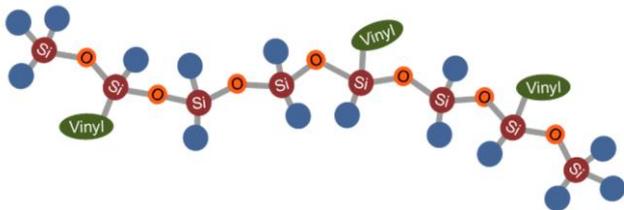

Fig. 7: The structure of PDMS. In blue: methyl (CH$_3$) groups. Vinyl (CH$_2$=CH−) groups can be introduced at some degree to initiate crosslinking [25].
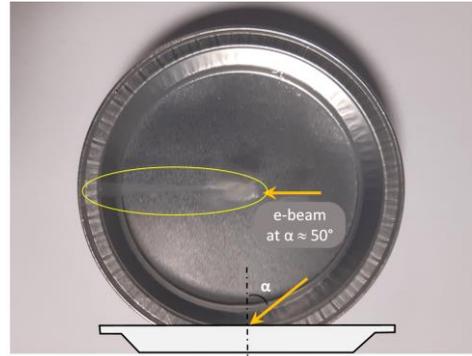

Fig. 8: The silicone gel sample surface after e-beam irradiation. The beam was impinging the surface as a small spot in the centre of the sample at an angle of 50° in respect to the normal to facilitate direct light detection. In yellow: the trace between the gun target position and the edge.

shown. By analogy with works on other polymers, the main emission was ascribed to polymer degradation, notably the possibility of having the formation of nanoclusters of carbon or Si. A picture of our sample after e-beam irradiation is shown in Fig. 8. The beam was applied with an angle of about 40° in respect to the normal of the film. A trace is clearly seen at the surface of the sample, as if the electron beam was directed to the edge of the sample put to the ground. There are two possible explanations for the phenomenon: either the build-up of the surface potential due to surface charging produces a deflection of the incident beam, or a surface current/discharge is formed to evacuate accumulated charges. The trace appearing on the surface strongly suggests that degradation occurred due to the beam, either through local heating under the beam or as a consequence of surface discharge propagation.

The short wavelength peak (325 nm) of the CL spectrum, Fig. 5c, appears consistent with the one obtained in photoluminescence and in some way would confirm the PL emission in this wavelength range for silicone gel. The position in wavelength does not fully match with the EL spectrum of Fig. 5a. Therefore, we cannot confirm that the EL spectra are characteristic of the material. Discharges could be occurring near the needle tips as a consequence of the high field produced here and possibly leading to damage and the formation of micro-voids. However, we cannot discard discharges occurring somewhere else in the assembly. In the same spirit, the signal recorded with the photomultiplier could be in part due to electromagnetic interferences (EMI) if PDs are active during acquisition. At the difference of the report by Anand et al [27], who investigated PD activity by electrical and optical detection in claimed EMI-free conditions, using the same PM, our set-up is not completely immune to EMI.

4. CONCLUSIONS

A first conclusion is that silicon gel is a very weakly luminescence material considering the compound investigated here. However, when submitted to an electron beam, a very strong luminescence signal appears, at a maximum of 595 nm. This emission was linked to material degradation, with possible formation of silicon nanoclusters. Silicone gel seems to produce a weak fluorescence at 325 nm detected by photoluminescence and cathodoluminescence.

A configuration has been tested for investigating the EL from silicone gel under divergent field. The response obtained, consisting in changes in the EL phase pattern when increasing

the applied voltage, and weak light emission with maximum at 350 nm, is not consolidated enough to derive firm conclusions. Discharges could be occurring not necessarily at the expected place (tip of the needles). Extra work is necessary to fix possible artifacts. The increase in stress frequency can be a way to improve the integral luminescence intensity without applying too high voltages, thus staying in discharge-free conditions. Working under secondary vacuum was attempted but was not straight-forward as the gel tends to outgas and spoil the vacuum level. In next steps, it is planned to attempt to work under uniform field using a cell dedicated to soft materials.

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