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# Charge transport in a Filler-free Silicone Rubber: Exploring Non-Linear Mechanisms and the “Liquid-like” Anomaly.

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**Abstract**— The literature diverges about the understanding of DC conduction in elastomeric materials, as silicone rubbers, attributing the conduction whether to a solid or to a liquid one. In this study, three different liquid silicone rubbers (LSR) free of fillers are fabricated from the same bi-component raw material, but with different curing times and component proportions. They were submitted to current-voltage measurements at 40°C, with 1h polarization and depolarization cycles, from 1 to 10 kV. The current-voltage characteristics of a low cured sample presented a sub-ohmic profile. The sample cured and post-cured for a longer time presented an ohmic conduction. The non-stoichiometric material presented also an ohmic conduction, but with a deviation to a sub-ohmic at higher voltages. Moreover, its reversal currents in the depolarization profile were characteristic of blocking activity. Analysis of conduction in rubbers is proposed to explain the liquid-like behavior for elastomers, and the solid-like appearance in certain cases.

**Keywords**—silicone rubber, LSR, DC current, conduction, polarization, depolarization, dielectric liquid.

## I. MOTIVATION

The use of silicone rubbers (SiR) in DC applications has been increasing considerably in the last years, with some sources already classifying this material as the third generation of elastomers for cable accessories and connections, right after the ethylene propylene rubber (EPR) and ethylene propylene diene monomer rubber (EPDM).

Nevertheless, the literature about its DC properties, especially the apparent conductivity ( $\sigma_{app}$ ) and space charge build-up, is highly contrasting: some sources identified mechanisms similar to most of solid dielectrics, with ohmic and super-ohmic conduction [1], [2], [3], while others have found the opposite of it, associating the electrical performance to those of dielectric liquids [4], [5], [6].

In fact, comparing the works in the literature is a challenge itself because the structure and the microstructure of the silicone rubbers is not always disclosed. As “silicone rubber” is only a class of elastomers, it covers a large variety of materials that change according to:

- The chemical structure: Most of the works seem to deal with the polydimethylsiloxane (PDMS), named MQ according to the ISO 1629 nomenclature. But the polymethylvinyl (MVQ) is also applied in electrotechnic, with the vinyl playing the role of crosslink site.
- Raw material consistency: The fabrication of an HCR (High consistency rubber, or heat curing rubber) is different from the LSR (Liquid silicone rubber).

- Curing technique: the RTV (room temperature vulcanized) is supposed to be different than an HTV (high temperature vulcanized).
- Filler content: industrial grades usually contain pyrogenic silica, and this silica is not always characterized. If nanosized, they provide a nanocomposite that should not behave as microcomposites.

In this work, we attempt to give insights about some of those contrasting features of the silicone rubber by molding and testing a specific LSR without fillers. The objective is to isolate the events coming from the matrix.

## II. MATERIALS AND METHODS

### A. Raw material

The material of study is the LSR Lumisil 7601 A/B (Wacker). It is an injection-molding high transparent grade developed for optical applications. Structurally, it is a polymethylvinyl siloxane (MVQ type), free of fillers and pigments or dyes, cured at high temperatures (HTV). The raw material has two components, each containing the base polymer. Component A includes the platinum catalyst, while the component B contains the crosslinker and a catalyst inhibitor.

### B. Fabrication procedure and sample preparation

Despite the recommendation for injection molding, plates have been fabricated through gravity casting molding under vacuum with homemade metal frames.

At room temperature, the components dosed in 50%/50% fractions have been manually mixed in a Beaker for 3 minutes, degassed under vacuum until no bubbles could be identified (Fig. 1 (a)), then transferred to a Kitasato glass. The mixture was poured under primary vacuum at room temperature on a mold with a square opening as showed in Fig. 1(b). The internal mold surfaces were coated with a thin, layer of neutral detergent, helping in the demolding.

After molding, the mold set is transferred to an oven previously heat at 165°C.

A first set of samples was heated for 20 minutes, giving 1-mm thick samples without post-curing. A second set was cured for 2 hours at 165°C, with additional 4 hours at 200°C as post-curing step (Fig. 1 (c)). A third set out of stoichiometry was fabricated like the second, but with an excess of component B (See Table I).

At the end, the plates were shaped into 70 mm diameter disks. They were conditioned in an oven under vacuum at 70°C for 2 days to dry, and then placed inside climatic

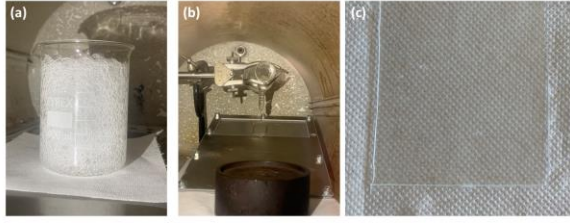


Fig. 1 Mixture under degassing step (a), mixture pouring into the mold under vacuum at room temperature (b), final 1-mm thickness plate without apparent imperfections (c).

TABLE I. RESUME OF SAMPLE PREPARATIONS

Sample code	A/B proportion	Curing procedure
1	50/50	20 min at 165°C
2	50/50	2 h at 165°C + 4 h at 200°C
3	25/75	2 h at 165°C + 4 h at 200°C

chambers for one week (40°C and 90% RH). The sample's weight variation through the whole conditioning procedure was smaller than 1 mg, which is our analytical balance sensibility (Ohaus Explorer), indicating no measurable water absorption or desorption.

Prior to the test, the disk surfaces were sputter-coated with 200-nm layer of gold using a turbomolecular pumped coater (Quorum Q150T ES).

### C. Electrical tests

The current density ( $J$ ) is obtained from current-voltage measurements. The set-up consists of a metallic cell with a plane-plane electrode system attached to its top cover. Openings and connections on the top gives the possibility to install RH probes and a thermocouple (Fig. 2). Once samples are installed, the cell is placed inside a climatic chamber and connected from one side to a high-voltage source (PS365 SRS High Voltage Power Supply) and on the other side to an electrometer (Keithley 6517B Electrometer/High Resistance Meter). All measurements were done at 40°C. Electric fields vary between 0.5 to 10 kV/mm. The test protocol consisted of polarization and depolarization (PDC) cycles of 1-hour. More information can be found in [7].

At least two samples of each LSR have been tested separately at opposite polarities (one at positive, and another at negative). Discrepancies between results obtained at opposite polarities were found to be up to 1.5 times the measured value. The results presented in this paper represent the average of these measurements.

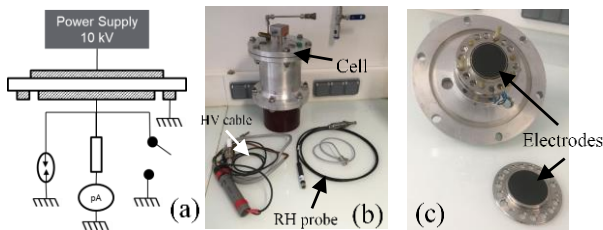


Fig. 2 Scheme of electrical tests (a); external view of test cell (b); view of electrodes arrangement (c).

## III. RESULTS

### A. Time-dependent currents.

The absorption currents measured in the LSR 1 showed similar patterns, none of them achieving the steady state, and some of them (above 3 kV/mm) presenting a specific transient current in the first 100s. On the other hand, the LSR 2 and 3 (Figs. 4 and 5, respectively) are more stable at the end of the first hour; both of them having similar patterns, the magnitude of the LSR 3 being two orders of magnitude higher than the LSR 2.

The resorption currents  $i_{res}$  (represented in Fig. 6 for  $V = 5000V$ ) do not reproduce the same profiles of the absorption ones. Because the values of the resorption currents at the end of the first hour are two orders of magnitude lower than the correspondent absorption ones, the sum  $i_{abs} + i_{res}$  at the end of the 1 hour gives  $i_{abs}$ . The resorption currents show distinct mechanisms: the LSR 3 present a current reversal after 230s of discharge, and another one at  $t = 2500s$ .

### B. Voltage-dependent currents.

Putting all the LSR in perspective with respect to the I-V characteristics by taking the quasi-steady state current value at the end of the first hour (Fig. 7), the slope of 0.5 has been found for the data of LSR 1. At the same voltage range, the LSR 2 and LSR 3 showed a slope  $\approx 1$ , that could be attributed to an ohmic conduction. Nevertheless, the last datapoints of

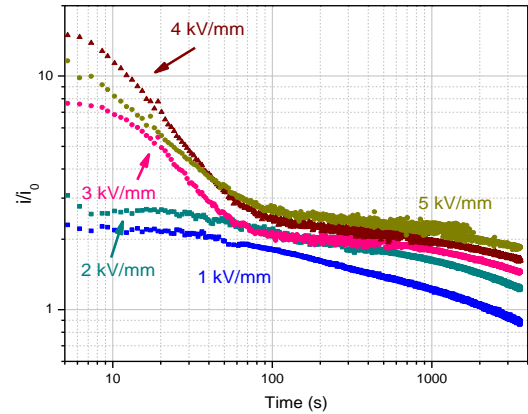


Fig. 3 Relative absorption current-time profile for the LSR 1.

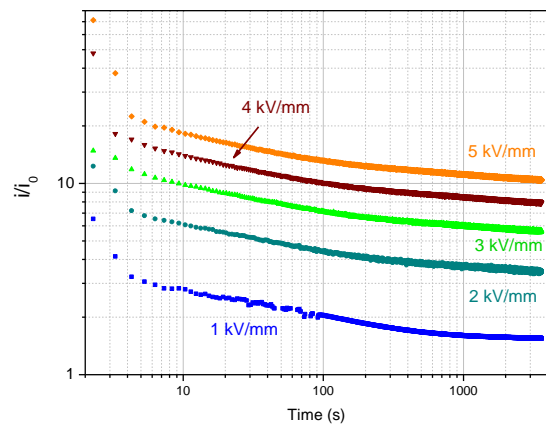


Fig. 4 Relative absorption current-time profile for the LSR 2.

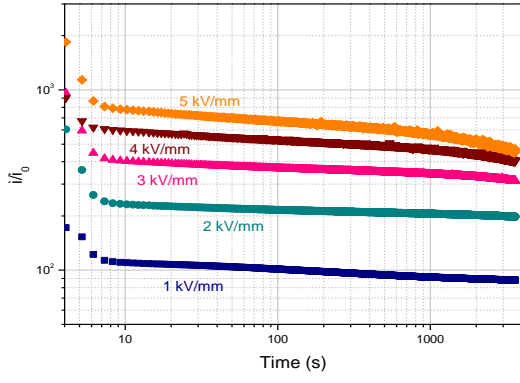


Fig. 5 Relative absorption current-time profile for the LSR 3.

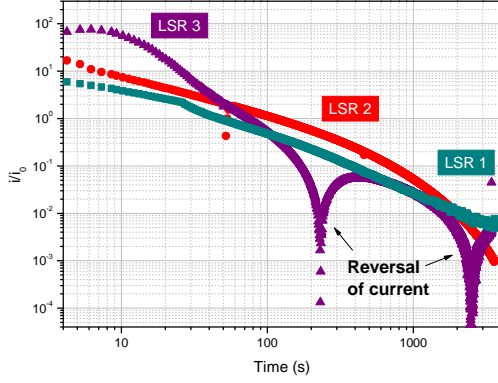


Fig. 6 Relative resorption current-time profile for all LSR after application of  $V = 5000$  V.

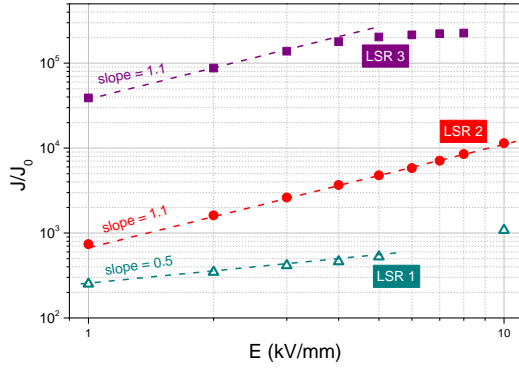


Fig. 7 Relative current-voltage characteristics for all the LSR.

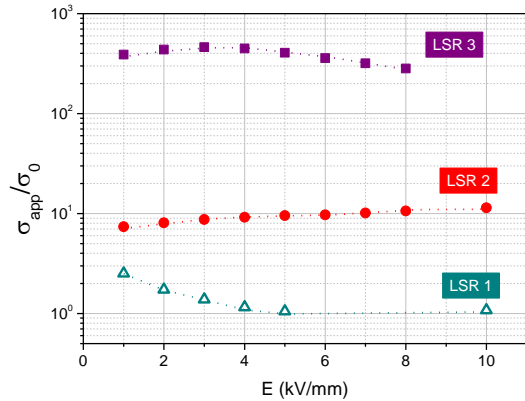


Fig. 8 Apparent conductivities for all the LSR.

the LSR 3 (from 5 to 10 kV/mm) sign a depletion and deviate from the ohmic model.

#### IV. DISCUSSIONS

The supplier recommends a curing process of 15 minutes under  $165^\circ\text{C}$ , but since our procedure is not the injection-molding and the molds were not pre-heated, the 20 minutes at  $165^\circ\text{C}$  was not enough to proper reticulate the material. The center of the plate was yet viscous. Thus, the LSR 1 represents an uncompleted cured sample, metastable, and anisotropic, whereas more time have been giving to cure the LSR 2 and 3.

##### A. From incompleto to completed curing.

The current-time profiles of the LSR 1 are similar to those found for dielectric liquids in which the transient current would be associated to ionic processes [8]. The J-E slope indicates the control by kinetics of charge generation observed for low-polarity liquids [9].

Delve into the liquid correlation, assuming that the first transient is due to ionic mobility, a transient time  $\tau$  can be determined at the inflexion point, corresponding to the time of flight (TOF) in which the carrier achieve the electrodes, with the mobility calculated according to equation 1. Results are summarized in table II and assign values considerably lower than dielectric liquids [10], [11].

$$\mu = d/(\tau.E) \quad [1]$$

The slope of 0.5 in Fig. 7 has no physical meaning. As a matter of fact, the J values were obtained following the classical method by the sum of the charging and discharging currents, each after one hour, but do not in fact correspond to quasi-steady states. They cannot describe a conduction model.

One can argue that the sample reticulate during the test, but the test temperature ( $40^\circ\text{C}$ ) is below the curing one ( $165^\circ\text{C}$ ).

Results of the LSR 2 show a higher current, with a conduction mechanism looking like an ohmic one. In a first glance, there is no evidence to assert that LSR 2 behaves as a liquid dielectric. Therefore, no TOF can be assigned.

##### B. From stoichiometric to non-stoichiometric formulation.

When out of stoichiometry by an excess of hardener (LSR 3), the resorption current assigns reversal currents. This behavior has already been reported for high-density polyethylene [12], and cross-linked polyethylene [13]. There, it was considered a charge build up due to a partial blockage at the electrode region: as soon as charge is injected during the charging step, it would be trapped next to the interface. During charging, they create a counter-field that attenuates the applied field, but during discharge, they are not immediately

TABLE II. CALCULATED MOBILITY BASED ON THE TOF OF LSR 1

E (kV/mm)	$\tau$ (s)	$\mu$ ( $\text{m}^2/\text{V}\cdot\text{s}$ )
3	30	$1.10^{-11}$
5	15	$1.10^{-11}$

evacuated, thus creating a field in the same direction of the one formerly applied and producing a current in the same direction as the charging one. A blocking activity identified through space charge measurements have already been reported for LSR [14].

The current-time profile of LSR 3 did not suggest the same ionic-like transport as seen for the LSR 1. The conduction current being 2 orders of magnitude higher than in the LSR 1, it is attributed to electronic charge carriers. This electronic conduction is not excluded for the LSR 1, but the mobility would be attenuated in the liquid-like phase.

The current reversal was not observed at lower voltage levels, and its occurrence corresponds to the voltage levels in which the J-V profile deviates from the ohmic (Fig. 7). This deviation may also be attributed to the blocking activity of the charges confined close to the electrodes that attenuate the field in the cathode and reduces the injection.

None of the samples presented the super-ohmic conduction observed for HCR grades filled with silica [1].

### C. Theory of rubbery conduction

The classical approach differentiates conduction mechanisms for either liquids or solids, but polymeric materials can bear both of these physical states.

The amorphous phase is glassy below the glass transition temperature ( $T_g$ ), but above it, it is viscous and can assign to the material a rubbery state: it is the case of semi-crystalline polymers below the melting temperature of this crystalline phase ( $T_m$ ) and above  $T_g$ , elastomers above  $T_g$  and  $T_m$ , and thermosets above  $T_g$ . If the charge carriers travel mostly through the viscous phase, the electrical properties could be associated with high-viscous liquids.

This may be the case of elastomers, since the rubber can be seen, at ambient temperatures, as a high-viscous liquid stick together due to a loose molecular network.

The different fabrication methods explored in this study show that managing the rubbery state by changing the curing degree, the stoichiometry, allow us to modify the charge carrier nature responsible for conduction, so as its mobility, affecting the main conduction mechanism.

The more the reticulation degree, the lesser is the chain movement, the closest the material may fit the theory of conduction in solid dielectrics with a limited ionic transport and a conductivity associated with electronic charge carriers.

## V. CONCLUSIONS AND PERSPECTIVES

The current-voltage behaviour of three different LSR fabricated from the same raw materials (free of fillers) has been studied. For the same voltage levels, same compression forces during electrical test, and same temperature (40°C), the silicone rubber may look more or less like a non-polar liquid depending on its rubbery state, controlled structurally by fabrication parameters. In addition, the polarization and depolarization currents were not symmetric, contrary to most of polymeric dielectrics. An analysis of the rubbery conduction is proposed.

For instance, the I-V characteristics of the silicone rubber less reticulated presented a sub-ohmic behaviour. The grade red and post-cured for a longer time showed an ohmic conduction, and the one out of stoichiometry with an excess of hardener presented an ohmic conduction at lower voltages, and a shift to sub-ohmic at higher voltage levels.

Further studies may include the influence of the compression force on the elastomeric sample.

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