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Understanding the dielectric behaviour of insulating silicone elastomers for HVDC application: influence of the reinforcing fillers

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1 Introduction

From the electrical grid point of view, the consensus to achieve an energy transition calls for the integration of HVDC technologies within the existing HVAC grid. Therefore, some understanding of the behaviour of the different materials and systems under DC constraint in comparison to AC is needed. Focus on silicone elastomers is proposed here, which are used as insulating materials in cable accessories [1].

It is well known that silicone elastomers are necessarily reinforced to present satisfying mechanical properties [2], making them composite materials with a polydimethylsiloxane (PDMS) matrix. This study aims to evaluate the influence of the reinforcing fillers on the dielectric properties by comparing a reference elastomer and its filtered version, without fillers.

2 Samples and filtration

The material studied is a commercial LSR (liquid silicone rubber) reference for HVAC applications.

LSR materials come in two pre-polymers, commonly known as part A and part B.

For the filtration method [3], the pre-polymers were first dissolved in cyclohexane in a ratio 10 g for 100 ml. A centrifugation step followed with two cycles at 6000 rpm during 1h30min each. Then successive filtrations were performed with 0.45 μm , 0.2 μm and 0.1 μm filters. Finally, the solvent is evaporated in a Rotavap at 60 °C. The filtration is a long and low efficient process, taking 3 days for 4 g of filtered matrix. The filtration was validated by checking the absence of filler using TGA (thermo-gravimetric analysis) and NMR (nuclear magnetic resonance). It is generally accepted that the residual mass on a thermogram corresponds to the quantity of filler. In the case of silicones that crosslink by hydrosilylation, as LSR, the presence of the platinum catalyst leads to the ceramisation of the PDMS chains around the fillers [4]. Hence, only the pre-polymer does not contain the catalyst (part B) was measured. The difference between the residual masses shows the disappearance of the fillers after filtration as illustrated in Figure 1 (0.3 versus 22 wt%).

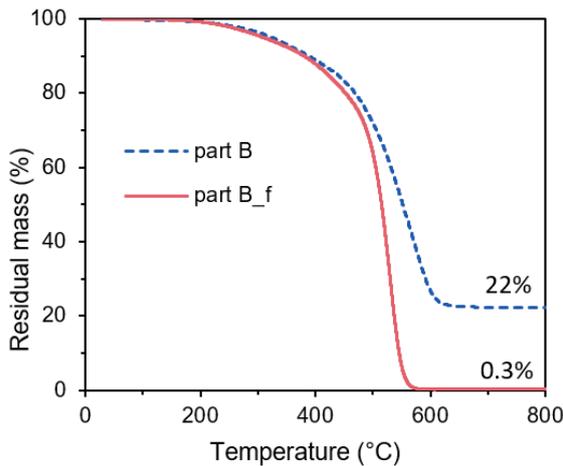


Figure 1: thermal degradation of part B and part B-f. Thermograms were carried out under nitrogen (N_2) at $10^\circ C/min$.

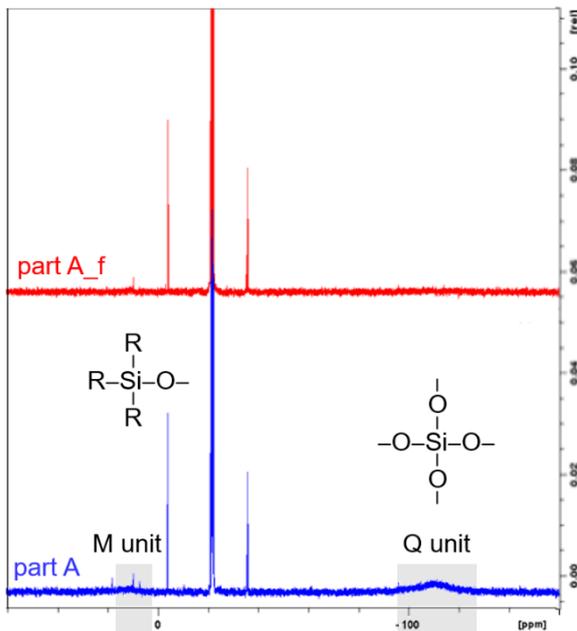


Figure 2: ^{29}Si RMN spectra of part A and part A-f. Same observations were done for part B.

^{29}Si NMR was also used to evaluate the filtration process and to get information on the nature of the filler, as presented in Figure 2. The samples are diluted in deuterated chloroform ($CDCl_3$), with tetramethyl silane (TMS) as a reference. The tubes are in quartz to prevent signal interference. The presence of Q units is clearly revealed in both part A and part B thanks to a broad peak at -110 ppm [5], and the presence of M units is also observed associated to a small broad peak at 10 ppm. The Q unit peak totally disappears on the filtered parts. So called “MQ” organic resins are therefore used as reinforcing fillers in the studied LSR.

For both the reference material and the filtered version, samples were processed by mixing the

two pre-polymers at 1:1 ratio and curing the blend (10min at $175^\circ C$ followed by 4h at $200^\circ C$). The reference material is poured into a 16 cm square mould of 1 mm thick. The filtered samples are made by a Dr Blade method, either on PTFE or aluminium support. Without the fillers, the mechanical strength is indeed not sufficient to obtain large films that do not tear. Given the very low filtration efficiency, we were only able to form a limited number of samples, with thicknesses ranging from 0.15 to 0.20 mm. Figure 3 shows some pictures of the filtered samples.

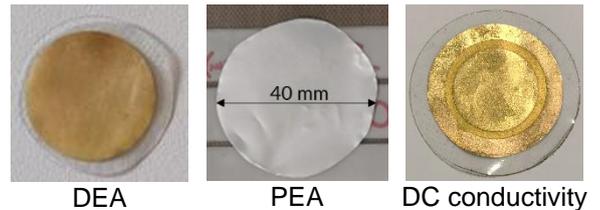


Figure 3: pictures of filtered samples.

3 Measurement protocols and results

Dielectric analysis (DEA)

Measurements were performed at room temperature applying $30 V_{rms}$ and from 10^5 to 0.1 Hz. Gold electrodes are deposited on both faces of the samples to ensure good electrical contacts and to guarantee the stressed volume. The deposition of electrodes is realised with gold sputtering and using a mask with a diameter of 30 mm. To compensate for the lack of guard ring and avoid measuring the contribution of potential bypass currents, the edges of the samples were surrounded with a PTFE tape.

DC volume conductivity

The DC volume conductivity is measured thanks to the dielectric spectroscopy module as source and femto ammeter, coupled with a high voltage amplifier. Given the multiplication factor ($\times 1000$), a safety system was put in place to manage the risks inherent to high voltage. The entire measurement chain is presented in Figure 4.



Figure 4: DC conductivity test bench. From left to right: ModuLab, sample holder, safety cabinet, voltage amplifier.

A guard ring connected to the ground is added to the previous electrode configuration to prevent any bypass currents. Table 1 presents the measurement parameters, that are adapted to the measurement sensitivity and capability for the reference LSR. Indeed, a larger and thicker sample was required to detect a current, leading to lower applicable electric field as the voltage source is limited to 1kV DC. The polarisation/depolarisation method with steps of 8 hours was used to obtain reliable results [6]. Measurements were carried out at room temperature.

Table 1: Samples and test parameters for DC conductivity measurements.

| | LSR | LSR-f |
|--------------------------------------|------------|-------------|
| Thickness (mm) | 1.17 | 0.19 |
| Electrode surface (cm ²) | 16.62 | 3.14 |
| Applied electricfields (kV/mm) | 0.5 ; 0.85 | 0.5 ; 2 ; 4 |

Space charge (PEA)

Space charge measurements on flat samples were carried out with the pulsed electroacoustic method (PEA). The system is placed in an oven to control the temperature. Electric fields up to 20 kV/mm at 30 °C were applied. The diameter of the high voltage (HV) electrode is 10 mm. The samples are wide enough (40 mm) to prevent flashover.

As said above for filtered samples, the polymer was “coated” on an aluminium (Al) foil, which allows the electrical contact at the bottom face (ground), and no metal coating was deposited on the top face (high voltage) to avoid an additional signal. Comparison on the reference material without Al deposition have been performed on the reference (not presented here). To the best of our observation, there is no significant impact of the Al coating on the PEA measurements.

Results

Analyses in the frequency domain show a decrease in permittivity from 2.8 to 2.5 at 50 Hz (Figure 5 on top). On the low frequencies area, a rise in the permittivity is observed for the filtered matrix due to electrode polarisation phenomenon. On the dielectric losses of the filtered sample, a slope is clearly visible (Figure 5 at the bottom), even from room temperature, and despite a range limited to 0.1 Hz at the lowest frequencies. This slope results in a plateau on the calculated AC conductivity at around 2.5×10^{-12} S/m (Figure 6). Although the slope is not equal to -1, it is close enough to assume that a contribution of conduction is observed on the filtered silicone [7].

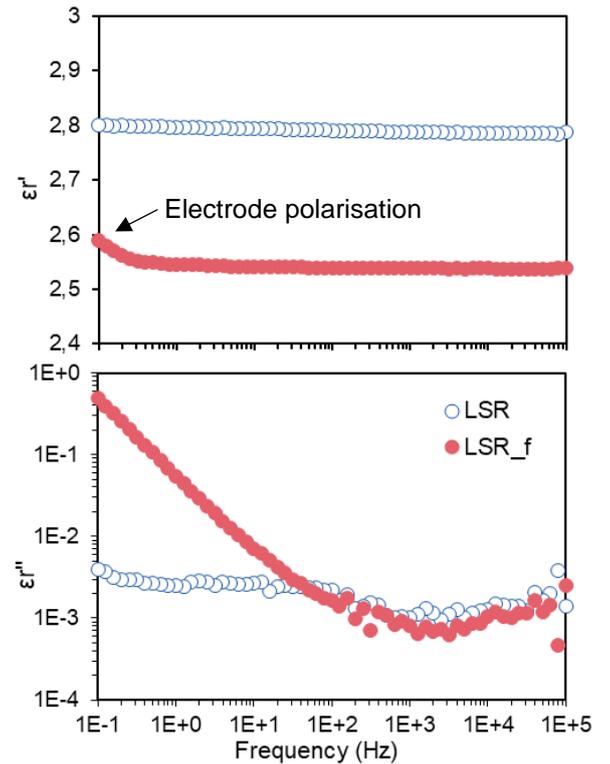


Figure 5: permittivity and dielectric of the reference (LSR) and the filtered version (LSR-f).

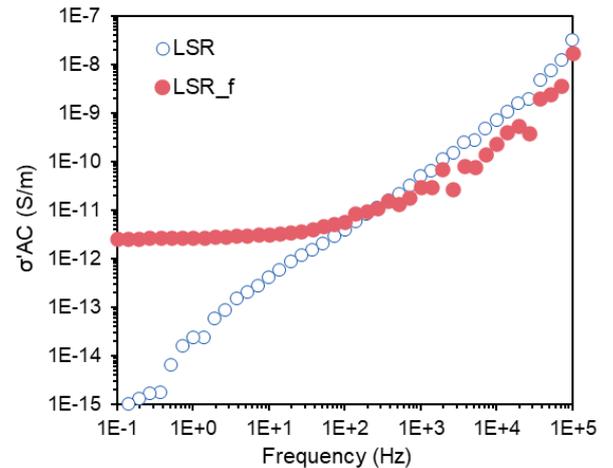


Figure 6: calculated AC conductivity of LSR and LSR-f.

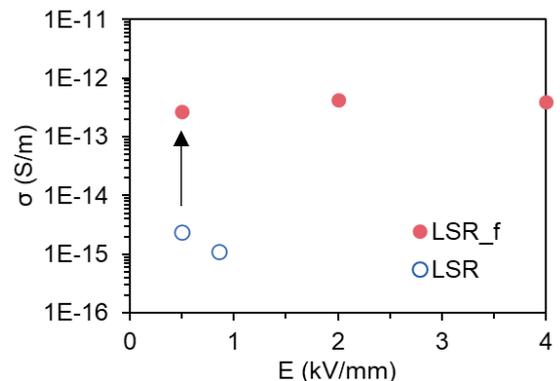


Figure 7: DC conductivity of LSR and LSR-f at room temperature.

DC volume conductivity results are shown in Figure 7 from different applied electric fields. The HVAC reference silicone exhibits at 0.5 kV/mm a conductivity of 2.4×10^{-15} S/m. In comparison, the filtered matrix presents a significantly higher conductivity of 2.7×10^{-13} S/m. An ohmic behaviour is observed for the latter, with a constant conductivity on the applied electric field range from 0 up to 4 kV/mm. With only two measurement points, it is unfortunately difficult to conclude on the slight decrease in the conductivity observed for the reference at 0.85 kV/mm.

Space charge measurements on polarization (voltage on) followed by depolarization (voltage off) sequence are presented in Figure 8 and Figure 9, at 5 kV/mm and 20 kV/mm respectively. We assume a detection threshold at $|0.1 \text{ C/m}^3|$.

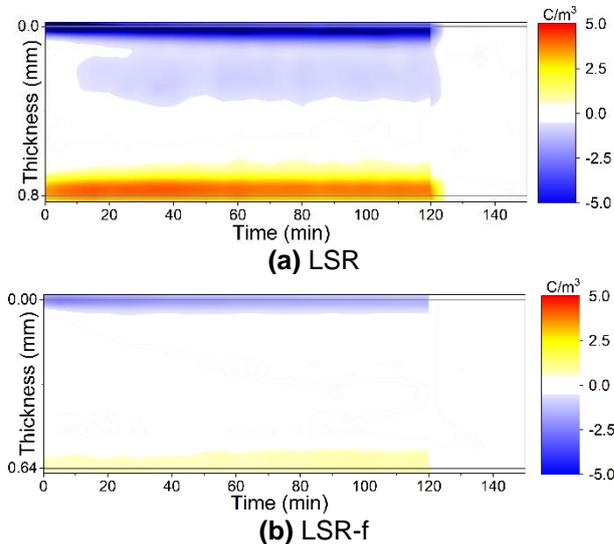


Figure 8: PEA signals for LSR and LSR-f on polarisation/depolarisation sequence at 5 kV/mm and 30 °C.

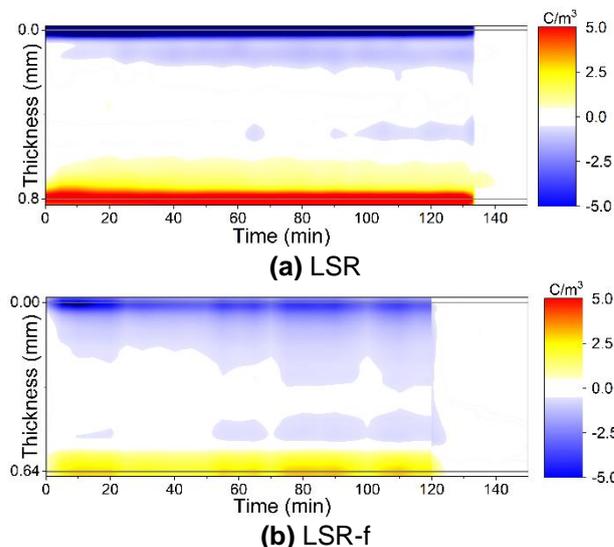


Figure 9: PEA signal for LSR and LSR-f on polarization/depolarization sequence at 20 kV/mm and 30 °C.

PEA graphs present the evolution of space charge in the sample thickness as a function of time. The detection electrode or anode (piezoelectric side) appears at the top of the graph. The high-voltage electrode (or anode) appears at the bottom. Positive charges are shown in red/yellow and negative charges in blue.

At 5 kV/mm and 30 °C during the 2 hours polarization phase, homocharges are observed [8]. The charge level is significantly higher for the LSR reference than for the filtered LSR. Given the very low intensity at the electrodes, for the latter, we assume it has no significant space charge. During the depolarization phase (only half an hour is shown), the fast disappearance of charges at the electrodes suggests shallow traps for the reference material [9].

At 20 kV/mm, the same trend is observed (note that the polarization of LSR is slightly longer than 2h): very marked homocharges in the reference, homocharges of low intensity in the filtered material and no deep trapped charges.

4 Discussion and Conclusion

The presented measurements highlight the difference in the dielectric behaviour of the reference material, which is filled with organic silicon resins and its filtered version, which no longer contains reinforcing fillers. The HVAC silicone reference can be considered as a nanocomposite as we assume the fillers to be nano-sized, the films being transparent. Dielectric spectroscopy measurements show that the presence of 22 wt% fillers increases the permittivity.

An even less intuitive but more marked change is observed on dielectric losses, with a conduction contribution on the filtered LSR. Although the frequency range is too limited to observe any AC conductivity plateau on the reference, this discrepancy is confirmed with the DC measurements for which an increase of two decades is observed between the samples. A significant increase in the number of mobile charge carriers effectively moving into the bulk of the filtered LSR can therefore be considered.

PEA measurements highlight the difference in space charge level in the two materials. In the reference material, homocharges i.e. "free" charge carriers that have been trapped, are observed very close to the electrodes. In contrast, no such charge trapping is visible in the filtered matrix. Charge carrier trapping therefore contributes to the lower conductivity value in the reference LSR. The nature of the fillers, as well as their concentration, have an important influence on the final properties in terms of space charges. At low concentrations, nanofillers are known to reduce the space charge and even reduce conductivity with conductive fillers [10]. At higher concentrations, nanofillers can result in lower space charges or more complex charge profiles [11].

In conclusion, we attribute the phenomenon of low conductivity of the HVAC reference material to the presence of fillers in high concentration. The interface between the matrix chains and the surface of the reinforcing fillers might acts as a trap for charge carriers. In the absence of fillers, and therefore of interfaces, the charge carriers further move into the volume, resulting in higher currents and DC volume conductivity. The study of surface modified fillers could confirm this hypothesis.

Understanding and illustrating this phenomenon can certainly help in formulating materials for HVDC applications, where field reinforcement phenomena due to space charge are feared.

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5 References

- [1] Ye, H., Fechner, T., Lei, X., Luo, Y., Zhou, M., Han, Z., ... & Li, D. (2018). Review on HVDC cable terminations. *High voltage*, 3(2), 79-89.
- [2] Paul, D. R., & Mark, J. E. (2010). Fillers for polysiloxane ("silicone") elastomers. *Progress in polymer Science*, 35(7), 893-901.
- [3] Roggero, A. (2015). *Analyse du vieillissement d'un adhésif silicone en environnement spatial: influence sur le comportement électrique* (Doctoral dissertation, Université Paul Sabatier-Toulouse III).
- [4] Delebecq, E., Hamdani-Devarenes, S., Raeke, J., Lopez Cuesta, J. M., & Ganachaud, F. (2011). High residue contents indebted by platinum and silica synergistic action during the pyrolysis of silicone formulations. *ACS Applied Materials & Interfaces*, 3(3), 869-880.
- [5] Li, R., Zhang, B., Sun, Y., Liu, B., & Wang, G. (2013). Synthesis of vinylphenyl oligomeric silsesquioxane based on MQ silicone resin. *Asian Journal of Chemistry*, 25(5), 2541.
- [6] Perez, A., Vu-Cong, T., Jacquier, F., Girodet, A., & Gentils, F. (2022, September). Influence of Stabilization Time and Post Processing Methods on the Accuracy of DC Conductivity Measurements. In *2022 IEEE International Conference on High Voltage Engineering and Applications (ICHVE)* (pp. 1-4). IEEE.
- [7] Kremer, F., & Schönhals, A. (Eds.). (2002). *Broadband dielectric spectroscopy*. Springer Science & Business Media.
- [8] Laurent, C. (1999). *Diélectriques solides et charge d'espace*. Ed. Techniques Ingénieur.
- [9] Tanaka, T. (2005). Dielectric nanocomposites with insulating properties. *IEEE Transactions on Dielectrics and Electrical Insulation*, 12(5), 914-928.
- [10] Hussain, R., Safarowsky, O., Hegge, J., & Hinrichsen, V. (2020, November). Development of a Liquid Silicone Rubber for the application in HVDC Cable Accessories. In *VDE High Voltage Technology 2020; ETG-Symposium* (pp. 1-6). VDE.
- [11] Chen, G., Li, S., & Zhong, L. (2015, July). Space charge in nanodielectrics and its impact on electrical performance. In *2015 IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM)* (pp. 36-39). IEEE.



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