Dielectric response of filled high temperature vulcanization silicone rubber

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ABSTRACT

The dielectric response of three kinds of filled high temperature vulcanization (HTV) silicone rubber – SiO2 based nanocomposite with different alumina tri-hydrate (ATH) micro-filler contents are investigated over a wide range of frequency and temperature. The results are analyzed in terms of the many-body Dissado-Hill dielectric response theory. In all three kinds of silicone rubber, a quasi-DC (QDC) process, a Dissado-Hill loss peak process and a diffusion process are observed. Specifically, the ATH filler contributes a QDC electrical transport/hopping process, which at higher temperatures causes the formation of a diffusion layer at the electrodes. The nano-SiO2 particles combined with rubber matrix give a Dissado-Hill loss peak dielectric relaxation. These two dispersion processes are shown to be associated with the interior interfaces of filled HTV silicone rubber. The effects of ATH filler content and temperature on the dielectric response are also analyzed in depth.

Index Terms — Dielectric response; HTV silicone rubber; Dissado-Hill theory; loss peak; quasi-dc; charge diffusion; interface

1 INTRODUCTION

Filled high temperature vulcanization (HTV) Silicone rubber is known to be an excellent outdoor insulation material resulting from its unique hydrophobicity transference and outstanding ability to withstand many kinds of environmental and electrical stresses [1]. Typically inorganic fillers such as silica (SiO2) and aluminum tri-hydrate (ATH) are added to the silicone matrix (polydimethyl siloxane, PDMS) to improve its mechanical properties and tracking/erosion resistance [2]. Since their dielectric properties are the major characteristic of insulation materials, their study is important for choosing the right material for a particular application [3]. The dielectric response is also used to obtain some detailed information of insulation materials at the microscopic scale [4]. By using the appropriate dielectric relaxation model [5, 6], the characteristics of the dipole and the mobile charge can be obtained, which help in the selection and design of insulation. Fillers play an important role in the overall performance of composite insulation, because many kinds of factors associated with the filler can affect the dielectric response [3], such as the type of filler, its concentration, the surface functionalization, etc.

Here, the dielectric response of a commercial silicone rubber containing SiO2 nano-filler with different ATH filler content is investigated and analyzed with the focus on the interior interfaces between the filler, nano-filler and polymer matrix.

2 THEORETICAL BACKGROUND

Structural relaxation in condensed matter can be understood as the reorganization of the relative orientations and positions of the constituent entities, including the molecules, atoms and ions [4], and can formally be thought of as the return to equilibrium following a thermodynamic fluctuation [5]. Where the relaxation involves a change in local strain a mechanical response will ensue and where the change involves a change in electric polarization a dielectric response occurs [4, 7]. Traditionally, the interpretation of dielectric response has been based on the concept of a system consisting of non-interacting relaxing entities, with these entities usually yielding a distribution of the parameters affecting the relaxation rate [8]. This concept can be found in the model of the Cole-Cole function [9], the Davidson-Cole function [10] and the Havriliak-Negami function [11]. However, rarely if ever can these empirical functions be related to the physical realities of the material structure [12]. In fact it is impossible for one entity to relax without affecting the potential structure of its environment and hence the motions of the other entities around it [4]. Since 1980 much effort has gone into attempting to include dynamic correlations/interactions into dielectric response theory [4, 7], which has shown that the relaxation follow a t^-n behavior (non-exponential decay) rather than an exponential decay behavior [13], as derived for the ideal case of non-interacting relaxing dipole entities and termed the Debye relaxation.
A small number of physically based theories have been proposed that take the interaction/correlation effect between the relaxing entities into account [5, 7, 14, 15]. Of these the Dissado-Hill theory [5, 16] is the most sophisticated and describes dielectric relaxation with parameters that have definite physical meanings [12]. This theory describes the dielectric response for two basic situations; one is for permanent dipole relaxation [5], and the other one is for relaxation due to mobile charge separation over restricted ranges [6, 17]. The former one is termed the Dissado-Hill loss peak model and the latter one is termed the quasi-DC (QDC) model. In these two models it is assumed that the structure of condensed matter is composed of clusters, where a cluster can be understood to be a spatially limited region with a partially regular structural order of individual units that are dynamically connected. As a result the relaxations of the appropriate entities (dipoles or charges) are “clustered” together instead of being treated as independent. The dielectric response of solids and liquids are thus result of the dielectric materials. Specifically, the definition of index \( n \) is determined by the correlation of these motions in the average cluster and will be less than unity because the relaxing entities within the cluster do not possess full translational symmetry. In the inter-cluster motion, the motion of a relaxing entity in one cluster correlates/couples with/to the relaxing entities in the other clusters. This kind of coupling can be caused by local structural distortion which can lead to an inter-cluster exchange of dipole orientation, when dipoles in one cluster couple their motion to dipoles in another cluster or equivalently the relaxation of dipoles in one cluster alter the equilibrium positions of dipoles in another cluster. The correlation coefficient for the inter-cluster relaxation exchanges is given by \( m-1 \). Because of the inter-cluster exchanges any selected cluster will possess a structure which is continuously varying in time. A macroscopically sized system of clusters can therefore only be described by a steady-state distribution, whose shape is governed by the value of \( m \) [5].

The indices \( n \) and \( m \) are related to the structural regularities of the dielectric materials. This means that the indices \( n \) and \( m \) of the shape function describe the microscopic morphology of the dielectric materials. Specifically, the definition of index \( n \) indicates that small values of \( n \) correspond to a highly disordered cluster, i.e. irregular structure, and large values of index \( n \) correspond to a highly ordered cluster, i.e. regular structure.

\[
\chi^\prime (\omega) = \chi(0) F(\frac{\omega}{\omega_p}) 
\]

(1)

Here \( \chi(0) \) is the magnitude of the susceptibility dispersion i.e. the dielectric increment for the single process of relaxation, and \( F(\omega/\omega_p) \) is the spectral shape function for this process with the frequency of the electric field \( \omega \) normalized by the characteristic frequency \( \omega_p \) of the particular relaxation process.

### 2.1 DISSADO-HILL LOSS PEAK MODEL

In the Dissado-Hill loss peak model, the spectral shape function has the form:

\[
F(\frac{\omega}{\omega_p}) = F_0^{-1} \left[ 1 + i \frac{\omega}{\omega_p} \right]^{n-1} 
\times \left[ F(1-n,1-m;2-n;1+i \frac{\omega}{\omega_p}) \right]^{-1} 
\]

(2)

\( F_0 \) is the normalizing parameter [7], with \( 0 \leq n < 1 \), \( 0 < m \leq 1 \), and

\[
F_0 = \frac{\Gamma(2-n)\Gamma(m)}{\Gamma(1+m-n)} 
\]

(3)

Here \( \Gamma(\cdot) \) is the gamma function and \( _2F_1(a,b;c;z) \) is the Gauss hypergeometric function [18]. With equation (2) for \( F(\omega/\omega_p) \) the components of the complex susceptibility ( \( \chi^\prime(\omega)=\chi(\omega)-i\chi^\prime\prime(\omega) \) ) have the following asymptotic frequency dependencies [7, 8]:

\[
\chi^\prime\prime(\omega) \propto \chi(0) \propto \omega^{n-1}, \omega \gg \omega_p 
\]

(4)

\[
\chi^\prime(\omega) \propto \chi(0) - \chi^\prime\prime(\omega) \propto \omega^n, \omega \ll \omega_p 
\]

(5)

Equation (1) and equation (2) describe completely the information contained in the dielectric response by means of four parameters, i.e. the characteristic frequency of the loss peak, \( \omega_p \), the amplitude of the susceptibility, \( \chi(0) \), and two shape parameters \( m \) and \( n \). The amplitude \( \chi(0) \) reflects the concentration of the relaxing dipoles that give the response. The loss peak frequency, \( \omega_p \), refers to the reorientation of the cluster as a whole [5]. The indices \( m \) and \( n \) are used to describe the asymptotic frequency dependence of the shape function. These indices relate to the two types of dynamic relaxation processes that inevitably result from the division of the system of dipoles into clusters.

In the intra-cluster motions, the vibration of a relaxing entity is coupled to the motions of the entities within the same cluster. The index \( n \) is determined by the correlation of these motions in the average cluster and will be less than unity because the relaxing entities within the cluster do not possess full translational symmetry. In the inter-cluster motion, the motion of a relaxing entity in one cluster correlates/couples with/to the relaxing entities in the other clusters. This kind of coupling can be caused by local structural distortion which can lead to an inter-cluster exchange of dipole orientation, when dipoles in one cluster couple their motion to dipoles in another cluster or equivalently the relaxation of dipoles in one cluster alter the equilibrium positions of dipoles in another cluster. The correlation coefficient for the inter-cluster relaxation exchanges is given by \( m-1 \). Because of the inter-cluster exchanges any selected cluster will possess a structure which is continuously varying in time. A macroscopically sized system of clusters can therefore only be described by a steady-state distribution, whose shape is governed by the value of \( m \) [5].

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### 2.2 DISSADO-HILL QDC MODEL

A different kind of dielectric response has been identified experimentally in which no loss peak was produced in the imaginary part of the susceptibility. This has been described by the QDC model [6, 17] for the situation where dipolar charges are so weakly bound to their counter charge that they can separate and move as quasi-free ions below a certain frequency (or equivalently when the period of the applied field allows sufficient time for charge separation before field reversal). This form of response occurs when the charges can only move
effectively within limited/restricted channels [6, 19], which prevents them from becoming completely independent charge carriers such as would be found in DC conduction. The QDC process is a dielectric response resulting from charge hopping over restricted ranges [4, 6, 20], over paths that give rise to a fractal hierarchy of relaxation dynamics [21].

In the QDC model, the spectral shape function is given as:

$$F(\frac{\omega}{\omega_c}) = F_0^{-1}\left(1 + i \frac{\omega}{\omega_c}\right)^{n-1} \times F(1-n,1+p,2-n)\left(1 + i \frac{\omega}{\omega_c}\right)^{-1}$$  \hspace{1cm} (6)

$$F_0$$ is the normalizing parameter,

$$F_0 = \frac{\Gamma(1-n)\Gamma(1-p)}{\Gamma(1-p-n)}$$  \hspace{1cm} (7)

The asymptotic frequency dependencies of equation (6) are given by [6,7]:

$$\chi''(\omega) \propto \chi'(\omega) \propto \omega^{n-1}, \omega \gg \omega_c$$  \hspace{1cm} (8)

$$\chi''(\omega) \propto \chi'(\omega) \propto \omega^{-p}, \omega \ll \omega_c$$  \hspace{1cm} (9)

Here \(0 \leq n < 1\) as for the loss peak case, though typical values [6, 16] have \(n\) greater than about 0.6. In principle, \(0 < p < 1\), however the physics of the QDC process dictate values in the range 0.35 \(< p < 1\), and almost always \(p \geq 0.5\) [6,16,20]. A value of \(p = 1\) corresponds to an ideal DC conductivity in series with a real capacitance, by means of the relationship between real, \(\chi'(\omega)\), and imaginary susceptibility, \(\chi''(\omega)\) at low frequencies [4], resulting from the QDC response function, equation (6), namely \(\chi''(\omega) / \chi'(\omega) = \cot{(1 - p)x/2}\) \((\omega < \omega_c)\) whereas the same susceptibility ratio in the Maxwell-Wagner case is proportional to \(\omega\).

2.3 DIFFUSION BARRIER PHENOMENA

At very low frequencies the charge separation during an ac half-cycle can become as large as the sample thickness in finite sized samples. The charges can then form a diffuse electric double layer [22] at the sample surface next to the electrodes when it is not possible for them to be neutralized immediately as would occur in an ohmic contact. This is typical of insulating materials [4] where a concentrated layer of charge with opposite polarity to the charge the electrode charge called the Stern layer adsorbs on the electrode via Van der Waals’ and electrostatic forces. A diffuse layer of charge of opposite polarity to the Stern layer may be formed outside of the Stern layer by electrostatic forces. At the low frequencies where the double layer is established the charge concentration is often sufficiently large to cause the charge distribution to be uniform in space along planes parallel to the electrode and its relaxation to be determined by diffusion under a concentration gradient directed perpendicular to the electrode, rather than movement on the fractal path structure of the QDC mechanism. The dielectric response at these low frequencies will thus have the diffusion behavior \(\chi''(\omega) \propto \chi'(\omega) \propto \omega^{-2}\) [4, 20]. It may also be possible for the QDC behavior to go over to this form of response at high temperatures if the restricted paths of the charges go over to a spatially uniform distribution. If the charges in the double layer remain constrained to structured paths relaxation via a concentration driven random walk will yield a more general form of diffusion response:

$$\chi(\omega) = \chi_{\text{eff}}(1)i(\omega)^s$$  \hspace{1cm} (10)

Here the value of the exponent \(s\) is determined by the fractal dimension of the path and the exponent \(\theta\) defining the nature of the random walk [16,23] via the relationship between time \(t\) and the walk distance \(R\), i.e. \(t \propto R^{\theta+2}\), with the classical 3D result of \(s = \frac{1}{2}\) when \(\theta = 0\). Typically the diffusion of charge in complex systems is not perfectly classical and values of \(s\) within the range from about 1/3 to 2/3 can be observed [24, 25]. It should be noted that it is impossible to separate out an amplitude factor and a characteristic transport frequency for equation (10) unless additional information is available to relate the response to maximum and minimum charge displacements \((R)\) through the beginning and end of the single power law response range [26]. This is the case for all single power law dielectric responses.

3 EXPERIMENTAL

3.1 MATERIALS

The silicone rubber investigated was made using the high
temperature vulcanization technique. All the material have a commercial origin and have been stored for some time. The ATH micro-filler and the nano-filler were dried at 100 °C for 12 hours in order to remove absorbed moisture and dry the particle surfaces. Before processing a mixture of methyl silicone oil and hydroxyl silicone oil were added in a 1:10 ratio and the mixture of silicone and fillers was vulcanized in a mold at 160 degrees Celsius for 10 min. The raw rubber used in HTV silicone rubber is polydimethylsiloxane (PDMS) with a molecular weight in the range of 450–700 thousand and the fillers are nano-SiO2 and Alumina Tri-hydrate (ATH).

![Figure 1. Structural image of PDMS](image)

The molecular structural image of PDMS is shown in Figure 1. The main chain of PDMS consists of an alternating arrangement of silicon and oxygen atoms and the side chains of PDMS consists of a symmetrical arrangement of methyl groups.

The size of the nano-SiO2 filler was observed by TEM (JEOL 2010F) and shown in Figure 2. It was found that the diameter of the individual nano-SiO2 particles is around 10–20 nm, but they are often clumped together into larger structures, as shown in Figure 2(b). The size of the ATH fillers was examined by using a laser particle size analyzer (Mastersizer 2000) and the distribution of the diameter of ATH filler is shown in Figure 3. The diameter of most of ATH fillers is in the range of 1–10 µm.

In outdoor insulation, ATH filler is typically added in the order of 35–45 % by weight to the silicone rubber formulations [1, 2]. For this investigation three kinds of silicone rubber with different ATH filler content were prepared [27], which are named as ATH80, ATH100 and ATH120, with the numbers 80, 100, 120 referring to the parts of ATH per hundred parts by weight of PDMS. The nano-SiO2 content was 40 parts by weight per 100 parts PDMS for all samples. The details are given in Table 1.

![Figure 2. TEM photograph of nano-SiO2](image)

Table 1. Details of filled HTV silicone rubber.

<table>
<thead>
<tr>
<th>Composition (by weight)</th>
<th>ATH80</th>
<th>ATH100</th>
<th>ATH120</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>SiO2</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>ATH</td>
<td>80</td>
<td>100</td>
<td>120</td>
</tr>
</tbody>
</table>

Samples of the filled silicone rubber were cut in the form of circular slabs with a diameter of 80mm and a thickness of 2 mm. Before starting the dielectric measurement, the samples were cleaned with alcohol and deionized water and then kept in a desiccator at 90 degree Celsius to avoid absorption of atmospheric moisture.

### 3.2 EXPERIMENTAL PROCEDURE

The dielectric response of the filled HTV silicone rubber samples were measured by using a three electrode system, with a measurement electrode of diameter of 44 mm surrounded by a guard electrode of inner diameter 50 mm and outer diameter 60 mm to eliminate surface currents from the measurement. The three electrodes were made from gold plated brass and placed in a hermetically sealed metal test cell. Some desiccant was also placed in the cell in order to keep the sample dry during the measurement. The test cell was placed in a Genlab oven with a Eurotherm 2204 temperature controller, which kept it at the predetermined/target temperature within 0.5 °C. A Solartron 1255HF frequency response analyzer (FRA) with a Solartron 1296 dielectric interface [28] was used for the measurements. The magnitude of the applied ac voltage was set to 2.0 V rms, and the dielectric response was measured over the frequency range from 10⁻¹ Hz to 10⁴ Hz with 9 points per decade. At each frequency, the data were acquired over two cycles of integration. The dielectric response of the different samples was Measurements were made at four temperatures (20 °C, 40 °C, 60 °C and 80 °C) with a 7 hour delay between ending one run and starting another to make sure that the silicone rubber was in a thermally stable state at the measurement temperature.

![Figure 3. Diameters distribution of ATH filler](image)
4 EXPERIMENTAL RESULTS

4.1 CAPACITANCE MEASUREMENTS

The capacitance and loss of ATH80, ATH100 and ATH120 over the measured frequency range are given in log-log representation in Figure 4 for the stated temperatures. The solid dots represent the real capacitance, \( C'(\omega) \), and the open dots represent the imaginary capacitance, \( C''(\omega) \), i.e. the loss. The complex capacitance \( C'(\omega) \) can be related to the complex relative permittivity, \( \varepsilon'(\omega) \), and the complex relative susceptibility, \( \chi'(\omega) \), by

\[
C'(\omega) = C'(\omega) - iC''(\omega) = \varepsilon'(\omega) - i\chi'(\omega) = \frac{\varepsilon_0 \epsilon_0 \epsilon_0}{d} [\varepsilon'(\omega) - i\epsilon''(\omega) + \epsilon(\infty)]
\]

Here the frequency dependent relative complex permittivity is denoted by \( \varepsilon'(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \) with \( \epsilon(\infty) \) the “infinite” frequency relative permittivity. The complex relative susceptibility is \( \chi'(\omega) = \chi'(\omega) - i\chi''(\omega) = \varepsilon'(\omega) - \epsilon(\infty) \), and \( Ad \) is the geometrical sample factor. The frequency-independent “infinite” relative permittivity \( \epsilon(\infty) \) (as well as the capacitance at infinite frequency, \( C_\infty (C_\infty = \varepsilon_0 \cdot A/d \cdot \epsilon(\infty)) \) can be understood as the contribution to \( C'(\omega) \) of any physical process whose response is at higher frequencies than the measurement frequency window. It also includes the free space capacitance.

Figure 4 shows that there is a substantial dielectric dispersion below \( 10^{-2} \) Hz and that it is strongly temperature dependent with the dispersion moving to higher frequencies as the temperature increases. This means that the real component \( C'(\omega) \) increases with temperature at a fixed frequency in the dispersion frequency range. The loss component is dominated by the imaginary susceptibility from the dispersion over the whole frequency range and consequently also increases with temperature. At frequencies above the dispersion the real component \( C'(\omega) \) is dominated by the “infinite” capacitance \( C_\infty \), which can be seen to be temperature independent.

4.2 THE DIELECTRIC SUSCEPTIBILITY

A clearer description of the dielectric response can be obtained by converting the capacitance to the relative susceptibility (\( \chi'(\omega) \) and \( \chi''(\omega) \) in equation (11)), by first subtracting the infinite capacitance and then dividing by \( \varepsilon_0 \cdot A/d \). The results are plotted in Figure 5, from which it can be seen that in all the experiments the principal feature of the dielectric response is the QDC process for which the parallel real and imaginary asymptotic behavior as described by equation (9) is clearly observed. At the lowest frequencies and highest temperature, there is an indication of a decrease in the frequency exponent of the loss component which is evidence for the presence of a series diffusive capacitance element [20].

4.3 MASTER CURVE

A master curve of the susceptibility for all temperatures has been produced using the normalization technique [4, 20] (i.e. the frequency dependent susceptibility at different temperatures is brought into coincidence in a Log-Log plot), see Figure 6. The advantage of the master curve representation is that it eliminates the frequency shift due to temperature and emphasizes the parts of the dielectric spectrum that have a frequency dependence that is unchanged by temperature. The point “A” in figure 5 is used as a reference point, such that the horizontal translation of the moving trace/locus in the master
curve describes the temperature dependence of the characteristic frequency of the susceptibility, and the vertical translation gives that of the amplitude. The master curves for ATH80, ATH100, and ATH120 are given in Figure 6. These show that over most of the frequency range the response has a temperature-independent frequency dependence, but at the lowest frequencies it is dominated by a diffusive phenomenon [6, 29], which does not normalize together with the major part of the susceptibility at higher frequencies, i.e. it has a different temperature dependence.

In the frequency range where the susceptibility data from the different temperatures come into coincidence (10^{-3} to 10 Hz at T = 80 °C) there are two regions where the real and imaginary components are parallel to one another in the log-log representation, but with a different slopes. These are regions of constant phase angle response [16, 30], and the slope in the plot gives the fractional power x of the susceptibility frequency dependence $\omega^{-x}$. In the lower frequency region the frequency exponent is close to unity while that in the high frequency region is less than 0.5. This frequency dependence is what is expected from a QDC process, with the formation of a master curve.

**Figure 5.** Relative Susceptibility of filled HTV silicone rubber ATH80, ATH100, ATH120

**Figure 6.** Master curves of filled HTV silicone rubber ATH80, ATH100, ATH120, normalized so that the values on the axes are correct at T = 80 °C.
plot revealing the temperature independence of the QDC frequency exponents $p$ and $n$.

The susceptibility at frequencies above the QDC dominated region has real and imaginary components in excess of that contributed by the QDC. Furthermore it could not be brought into coincidence by the same frequency-amplitude shifts as that for the QDC. This means that there is an additional relaxation mechanism in this frequency region.

Since it was impossible to obtain a single master curve over the entire measurement frequency range it follows that the activation energies of the diffusion process, of the characteristic frequency of the QDC process, and the higher frequency loss peak relaxation are not the same, and hence the physical origins of these three processes are also not the same.

In addition to a shift in the characteristic frequency, $\omega_c$, of the QDC process the locus of the trace point in Figure 6 shows that there is a substantial increase in its amplitude with increasing temperature (note that the locus shows Log$_{10}$ of the inverse amplitude as a function of Log$_{10}$ of the inverse characteristic frequency). This means that the concentration of moving ions and their separation at a given frequency increase with increasing temperature.

As a result of the normalization in Figure 6 it is clear that the response contains several partially overlapping processes, each of which should be analyzed separately. The required decomposition of the total response into individual processes is achieved by means of an equivalent circuit in which each circuit element represents one of the processes. These are combined together so as to reflect the way the contributions of the different processes combine electrically within the material.

### 4.4 THE EQUIVALENT CIRCUIT FITTING

The dielectric response of a variety of materials can be analyzed in terms of a series of generalized impedances [24], for example, two impedances $Z_1$ and $Z_2$, as shown in Figure 7(a). Each generalized impedance may consist of a number of parallel connected dielectric response elements, $Z$, such as a DC conductance ($G$), a non-dispersive infinite-frequency capacitance ($C_\infty$), a QDC process capacitance (QDC), a Dissado-Hill loss peak capacitance (D-H) and a diffusive capacitance (Diff), as shown in Figure 7(b) where all the elements above are connected in parallel. For a specific dielectric material not all the dielectric response elements or generalized impedances are present, and the selection of the elements required should be related to the physics of the microscopic structure of the dielectric material.

The QDC response and D-H relaxation can be attributed to the bulk properties of the silicone rubber composite [5, 28] whilst the diffusion term relates to the formation of a double layer at an interface [29]. Thus the most general equivalent circuit model used in the following analysis is a two-layer structure consisting of two series-connected generalized impedances; one representing the double layer and the other representing the bulk dielectric behavior of the silicone rubber composite. The bulk properties are represented by a parallel connection of a QDC and a D-H impedance element together with a parallel connected DC conductance, $G$, and infinite frequency capacitance, $C_\infty$. The full two-layer equivalent circuit is only used for the response at $80 \, ^\circ C$ for which the
The diffusion process observed at 80 °C in all samples is interpreted as an electrode interface response. This is connected in parallel with an infinite-frequency capacitance, $C_2$, and both these interface circuit elements are connected in series with the generalized impedance representing the bulk response of the material, see the inset to Figure 9(b). It will be shown that all these elements have clear physical meanings related to the composition and microstructure of filled HTV silicone rubber.

Figure 8 shows the equivalent circuit fit to the response of ATH100 at 20 °C, 40 °C, and 60 °C, together with the decomposition into the contributions of each individual circuit element to the overall response. Table II gives the fitting parameters for each silicone rubber sample at every test temperature. The value of $p$ is the same for all temperatures as implied by the formation of the master curve, however the other shape parameters change slightly with temperature reflecting the deviation from a temperature-independent frequency dependence at high frequencies. The fitted values given in Table II and the component decomposition given in the figures show that the dielectric response of silicone rubber at low frequency is determined almost entirely by the QDC process, since the contribution of the dc-conductance is insufficient to dominate the dielectric response at any place in the measurement frequency range.

In Figure 9, a comparison is made of the fitting of the single layer model and the double layer model to the 80 °C experimental data that contains the diffusion response. The best fit to the single-layer equivalent circuit without the series diffusion (used for the lower temperatures) is shown in Figure 9(a) for the dielectric response of ATH100 at 80 °C. It can be seen that except at the very lowest frequencies, where the measurements are significantly less than the fitting curve, the fit is very good. Figure 9(b) shows that including a series impedance, comprising a diffusive element in parallel with a non-dispersive capacitance [29], in the equivalent circuit (as shown in the inset) improves the fit to cover the entire measurement frequency range. A non-dispersive capacitance component, $C_{2\infty}$, in parallel with the diffusion element is required because otherwise the diffusive component would result in a dispersion in the real part of the capacitance at high frequencies [4,29], which is not observed in the data. This behavior occurs when the diffusion phenomena only takes place in a small region a short distance from the electrode. The capacitance, $C_{2\infty}$, is therefore interpreted as the capacitance of the double layer that forms adjacent to the electrodes. The diffusive behavior occurring at low frequency therefore results from the charge build-up in the region near the electrodes. At temperatures below 80 °C it would be formed at frequencies below the measurement range used here.

## 5 DISCUSSION

### 5.1 THE PHYSICAL ORIGIN OF DISPERSION PHENOMENA IN FILLED HTV SILICONE RUBBER

A microscopic schematic of HTV silicone rubber is given in Figure 10, which shows that there are two kinds of interior interface. One is the interface between the ATH and the PDMS matrix, and the other one is the interface between nano-SiO$_2$ and PDMS.
These two kinds of interface can be expected to strongly influence the dielectric response of filled silicone rubber.

The QDC process is observed in a number of materials which possess an underlying similarity of structure. These are materials that possess limited length channels or interior interfaces (such as in granular materials [4]) which contain a number of binding sites that are partially occupied by ions [6, 20, 31] and whose structure has positions of contact between the interfaces that allow ion transfer between them. In general, there is no chemical interaction between the ATH filler and the PDMS matrix, so the combination of ATH filler and PDMS matrix mainly depends on their physical interaction. For this reason the interface between the ATH fillers and the PDMS matrix provides limited paths for the displacement of ions such as $\text{Al}^{3+}$ and $\text{OH}^{-}$ that come from the ATH filler particles. These ions will move in the interfaces between the ATH filler particles and the silicone matrix in the manner of a quasi-de behavior. In this situation, each ATH filler particle (or group of particles) provides a surface with $\text{Al}^{3+}$ and $\text{OH}^{-}$ ions that come from the ATH filler particles. These ions have the nature of a cluster in the QDC model. The inter-cluster transport results when ions are separated by transferring from the interface of one particle (or group) to that of another. The QDC process in filled silicone rubber can thus be considered to be mainly caused by the addition of ATH filler.

![Microscopic schematic of filled HTV silicone rubber](image)

**Table II.** Dielectric properties of filled HTV silicone rubber.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ATH80</th>
<th>ATH100</th>
<th>ATH120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td>0.64</td>
<td>0.68</td>
<td>0.73</td>
</tr>
<tr>
<td>40°C</td>
<td>0.64</td>
<td>0.68</td>
<td>0.73</td>
</tr>
<tr>
<td>60°C</td>
<td>0.64</td>
<td>0.68</td>
<td>0.73</td>
</tr>
<tr>
<td>80°C</td>
<td>0.64</td>
<td>0.68</td>
<td>0.73</td>
</tr>
<tr>
<td>QDC</td>
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</tr>
<tr>
<td>$\omega_{p}$</td>
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<td>$10^{-1}$ $10^{0}$ $10^{0}$ $10^{0}$</td>
<td>$10^{-1}$ $10^{0}$ $10^{0}$ $10^{0}$</td>
</tr>
<tr>
<td>$\chi(0)$</td>
<td>$5.08$ $4.12$ $6.87$ $1.25$</td>
<td>$5.29$ $5.27$ $7.90$ $1.35$</td>
<td>$5.83$ $5.32$ $8.29$ $1.53$</td>
</tr>
<tr>
<td>D-H loss peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>0.53</td>
<td>0.53</td>
<td>0.59</td>
</tr>
<tr>
<td>$n$</td>
<td>0.83</td>
<td>0.81</td>
<td>0.83</td>
</tr>
<tr>
<td>$\omega_{p}$</td>
<td>$10^{-1}$ $10^{-2}$ $10^{-1}$ $10^{-1}$</td>
<td>$10^{-1}$ $10^{-2}$ $10^{-1}$ $10^{-1}$</td>
<td>$10^{-1}$ $10^{-2}$ $10^{-1}$ $10^{-1}$</td>
</tr>
<tr>
<td>$\chi(0)$</td>
<td>$1.37$ $4.03$ $5.38$ $1.15$</td>
<td>$1.10$ $4.00$ $5.04$ $8.29$</td>
<td>$1.10$ $3.80$ $5.04$ $8.23$</td>
</tr>
<tr>
<td>Diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>0.33</td>
<td>0.38</td>
<td>0.34</td>
</tr>
<tr>
<td>$C_{2e}$ (pF)</td>
<td>1210</td>
<td>1328</td>
<td>2674</td>
</tr>
<tr>
<td>$G$(pS)</td>
<td>$7.6$ $1.0$ $1.7$ $1.9$</td>
<td>$9.8$ $1.9$ $2.2$ $2.4$</td>
<td>$1.2$ $2.8$ $2.6$ $2.8$</td>
</tr>
<tr>
<td>$C_{1e}$ (pF)</td>
<td>21.1</td>
<td>21.1</td>
<td>24.3</td>
</tr>
</tbody>
</table>

Figure 10. Microscopic schematic of filled HTV silicone rubber.
The main active group on the surface of nano-SiO$_2$ is the hydroxyl group, which can form hydrogen bonds with the PDMS backbone, as shown in Figure 11. Because there are Si-O bonds in both PDMS and nano-SiO$_2$ parts of the PDMS backbone is also regularly arranged around the nano-SiO$_2$. These two kinds of factors cause the nano-SiO$_2$ to combine well with the PDMS matrix [32, 33].

The chemisorption of the PDMS on the nano-SiO$_2$ can be expected to restrict the PDMS chain motions in this region. However nano-particles have a very large interfacial region [32] and PDMS chains further away from the particle may become free to move and contribute to the dielectric response [34]. In addition the interfaces will have a Gouy-Chapman double layer [34]. In an electric field movement of the charge carriers will lead to interfaces with a net charge, in a similar manner to a Maxwell-Wagner process [29]. Since the TEM picture (Figure 2) shows that the nano-SiO$_2$ particles are clumped together in a variety of structures we would expect the charging of each particle to interact with that of others and so the Debye peak of a classical Maxwell-Wagner process [3, 20] (originating with a single series resistance-capacitance equivalent circuit) would not occur and instead we would expect the response to have the more general frequency dependence of a D-H loss peak.

At low frequencies and high temperatures the QDC process causes charges to separate to the extent that the charge builds up an electrical double layer at the electrode. This will contribute a diffusive process to the response. The high value of the parallel capacitance $C_\infty$ (i.e. 1000-3000pF) in comparison to the amplitudes of the QDC and loss peak relaxation (0.1 to 1 pF), make it clear that the response in this frequency region originates from a thin layer at the electrodes. The value of the exponent $s$ (Table II) is less than the classical value of 0.5 and indicates that the charges move on defined paths, though the data is too limited to be certain of this.

5.2 THE EFFECT OF ATH FILLER ON THE DIELECTRIC RESPONSE OF SILICONE RUBBER

The capacitance of filled HTV silicone rubber originating from the response at frequencies above $10^4$ Hz ($C_\infty$ of Table II) increases with ATH content such that its value for ATH80, ATH100, ATH120 is 21.1 pF, 22.9 pF and 24.3 pF, respectively. Since the permittivity of ATH filler is larger than that of the silicone rubber base polymer [3] (i.e. the composite of PDMS and nano SiO$_2$), this would be the expected result of an additive mixture law for two-component systems [35].

The ATH filler also has a strong effect on the QDC process. At the same temperature the characteristic frequency and amplitude of the QDC process increases as the ATH concentration increases, see Table II. It can be expected that increasing the concentration of ATH particles will reduce the distance between adjacent ATH particles or particle clusters and hence make ion transport/hops between them easier and faster, thereby increasing $\omega_p$. Similarly increasing the ATH concentration can be expected to increase the joint surface area of ATH particle clusters and hence increase the supply of separable ions per cluster. It is also noticeable that the value of the exponent $p$ increases with ATH concentration suggesting that the fractal dimension of the ion transport paths joining the ATH particle surfaces have been modified to give a transport closer to the spatially uniform behavior of an ideal DC conductivity. All of these features associate the QDC process with charge transport between ATH filler surfaces on spatially restricted paths, and are consistent with the physics of the QDC model.

The effect of the ATH filler on the D-H loss peak is less marked than on the QDC process. Table II shows that at a given temperature the amplitude of the D-H loss peak is essentially independent of ATH filler concentration. This indicates that the response originates with effective dipoles in the PDMS + nano-SiO$_2$ matrix. However the characteristic relaxation frequency $\omega_p$ increases with ATH filler concentration. This would not happen if the response was just due to re-arrangement of a Gouy-Chapman double layer around the nano-particles. One possible explanation is that the increase in ATH filler concentration is plasticizing the matrix and thereby increasing the relaxation rate of molecular dipoles in the PDMS. Alternatively the ATH filler is supplying ions that charge the surfaces of the clumps of nano-SiO$_2$ observed in Figure 2. An increase in ATH concentration would then increase the charge carrier concentration, essentially increasing the effective conductance that charges the nano-SiO$_2$ surfaces. The fact that $\omega_p < \omega_c$ and that the exponent $n$ for both QDC and D-H loss peak have similar values suggests that the latter explanation is the more likely one. The stronger temperature dependence of $\omega_p$ (50:1 for $\Delta T = 60^\circ$C) compared to $\omega_c$ (10:1 for $\Delta T = 60^\circ$C) is consistent with an explanation in terms of ions from ATH particles moving through the PDMS matrix to charge the nano-SiO$_2$ surfaces. However the temperature dependence of the loss-peak amplitude is difficult to explain in this way, see Table II where a ratio of about 8:1 for $\Delta T = 60^\circ$C is found. Consequently an explanation in terms of relaxing molecular dipoles in the PDMS matrix cannot be ruled out without experimental data showing its absence in a PDMS matrix without any ATH.

5.3 THE EFFECT OF TEMPERATURE ON THE DIELECTRIC RESPONSE OF FILLED HTV SILICONE RUBBER

The shifts along the Log(frequency) axis required to bring the QDC response into coincidence in the master curve plots of Figure 6 give the shift in the characteristic frequency of this response and can be used to determine its activation energy. An Arrhenius plot of the characteristic frequency, taken from the

$\Delta$
temperature shift points of figure 6, is presented in Figure 12. The data exhibits a good fit to a thermally activated process and the activation energies of the QDC characteristic frequencies determined from the slopes [36] of the straight lines is given in the inset. It can be seen that the activation energy decreases on increasing the ATH filler content reflecting an increased ease for the ions to be separated consistent with a reduction of the distance between ATH particle clusters.

The amplitude of the QDC process is also dependent upon temperature. An Arrhenius plot constructed from the logarithm of the shift along the amplitude (y-axis) in the master curves of Figure 6, is given in Figure 13. It can be seen that the amplitude has a good fit to a thermally activated process, and that the activation energy (0.24eV) is independent of the ATH concentration. This indicates that the ease of release of ions from the body of the ATH particles onto their surface is a property of the particle and independent of the particle clustering. However the amplitudes themselves increase with ATH content (see Table II) thus the concentration of ions available for the QDC transport must be dependent upon the concentration of ATH particles (i.e. total surface area) in the clusters that feed the transport paths.

The characteristic frequency and amplitude of the D-H loss peak also increases with temperature, and activation energies can be obtained from the fitted values given in Table II. For example, a value around 0.55 eV can be estimated for the characteristic frequency $\omega_p$. However there is uncertainty in the fitting so any values derived should be taken as a guide to the magnitude rather than an exact value.

From the fitting process, it can be found that in the high frequency region of our observation window the susceptibility of filled silicone rubber is determined by the additive combination of the intra-cluster motion of the QDC behavior and of the Dissado-Hill loss peak behavior (as shown in Figure 8(c)). The steepness of the frequency dependence in the Log-Log representation of the susceptibility is determined by the value of $n$ in the Dissado-Hill model. It can be seen from Table II that $n$ decreases with increasing temperature for both processes, which would give a greater dependence upon frequency in this region. However the frequency dependence at frequencies of $10^3$ Hz and above is sensitive to the value of $C_{\infty}$ subtracted to obtain the susceptibility and hence changes in $n$ must be treated with some caution.

The very low frequency diffusive response can only be observed in our frequency window at high temperatures when the QDC charge transport mechanism is fast enough to charge the electrode interface at frequencies of $\approx 5 \times 10^{-4}$ Hz. At lower temperatures this will not happen until the frequency is below $10^{-4}$Hz.

6 CONCLUSIONS

It has been shown that the Dissado-Hill many body theory of dielectric relaxation can give a detailed interpretation of the dielectric response of a commercial filled silicone rubber based on the microstructure of the material. In the frequency window and temperature range used in this study, three kinds of dispersion processes can be observed: i.e. a QDC process, a Dissado-Hill loss peak process, and a diffusion process. The QDC process is caused by the ions (Al$^{3+}$, OH$^-$), originating from ATH filler particles, which hop through the PDMS matrix between the ATH filler-matrix interfaces. This allows charge transfer between ATH particles or particle clusters on structured paths provided by the ATH particle system. The Dissado-Hill loss peak process originates with effective dipoles in the PDMS + nano-SiO$_2$ matrix. Its most likely origin is with interfacial polarization between nano-SiO$_2$ and PDMS. A diffusion process is observed at low frequency and high temperature that is caused by the formation of an electrical double layer at the electrodes. Higher ATH content increases the amplitude and characteristic frequency of the QDC process, but decreases the activation energy of the characteristic frequency without affecting that of the amplitude. It also results in a higher value of the frequency power law exponent $p$ in the QDC process that can be associated with changes to structured paths provided by the ATH filler microstructure. These results show that there can be a considerable increase in finite range charge transport and bulk charge storage when filler particles are introduced into insulating materials in the large quantities required for their commercial application.

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REFERENCES


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