Dielectric Response of Nano Aluminium Tri-hydrate Filled Silicone Rubber

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ABSTRACT: The dielectric response of a nano-ATH (Aluminium Tri-hydrate) filled silicone rubber is investigated over the frequency range 10^{-4} to 10^3 Hz and compared with that of the micro-ATH composite. An equivalent circuit has been used to decompose the dielectric response into: a loss peak process, a quasi-dc (Q-DC) process, a dc-conductance and constant high frequency capacitance. It was found that the Q-DC and loss peak were a result of the ATH filler with the loss peak more clearly resolved in the nano-ATH filled material than in the micro-ATH material where it is weaker and partly obscured by the Q-DC process. In contrast to the micro-ATH material the characteristic frequencies of all the dielectric responses in the nano-ATH filled samples have the same activation energy. The physical mechanisms of the Q-DC process and loss peak are discussed in terms of long range transport between nano-ATH clusters and the dipolar behavior of isolated clusters respectively.

*K*eywords**:** A. Polymer-matrix composites, A. Nano particles, B. Electrical properties, B.

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Interface, B. Transport properties.

1. INTRODUCTION

Recently some attention has been paid to silicone rubber nano-composites for use as dielectric elastomer actuators using high permittivity nano-particles (BaTiO$_3$ [1]) or conducting carbon nano-tubes [2]. Here our focus is on silicone rubber for macroscopic outdoor insulation where the filler particles are non-conducting and have a permittivity similar to that of the rubber. Silicone rubber has largely replaced ceramics as outdoor insulation mainly because it exhibits a good anti-pollution flashover performance [3,4] and can be filled with micro-particles of aluminium tri-hydrate (ATH) that improves resistance to tracking and erosion through their ability to release water at elevated temperatures [5,6]. The drawback to the use of micro-particles is that they tend not to be spherical and this is known to lead to a reduced electrical breakdown strength when they are used as fillers in insulating dielectrics such as epoxy resin [7]. An alternative is to use nano-particles, which have been shown to increase the breakdown strength of filled epoxy resin with respect to the micro-composite and when uniformly dispersed even increase it above that of the unfilled material [8]. An additional advantage is that nano-fillers are known to reduce the formation of field-distorting space charge in DC fields [9], which limits the inception of potentially damaging processes and facilitates system design for DC usage. The replacement of micro-ATH filler by nano-ATH particles would therefore appear to present significant advantages for the performance of the silicone rubber composite. However most of the nano-composite dielectrics that have been studied to date have a nano-particle filler concentration that is less than 10% by weight and thus good mixing techniques can produce composites with a near uniform distribution of particles [8]. This is not suitable for the

purpose of outdoor insulation since the ATH particles are present to ameliorate heat generating processes and are thus required in substantial concentration and particle agglomeration is inevitable [10], although even when agglomerated nano-particles can lead to a better breakdown strength than the micro-composite [8]. The agglomeration will however lead to the possibility of long range charge transport since the ATH particles can act as a source of ionic charge carriers such as Al^{3+} and OH^{-} and these may transport considerable distances via percolation as found in the micro-composite [10]. Transport currents of this type give a frequency dependent dielectric response [11] and can lead to dielectric heating and internal redistribution of high field regions when the insulator experiences high applied fields, which would be particularly damaging when the applied fields are rapidly varying. Such conditions occur, for example, when the insulation is subjected to internal partial discharges or surface flashover. Because of the thick interphase regions that exist around nano-particles in polymeric composites relative to the particle size [12-16] it is likely that the dielectric response in nano-composites will exhibit some differences from those observed in the micro-composite [10]. Since silicone rubber micro-composites have been commonly characterized through their dielectric response [17, 18] this approach will be adopted here to compare the nano-composite to the micro-composite.

2. EXPERIMENTAL

2.1. MATERIALS

Investigation of three different composites are reported. Their composition and sample nomenclature is given in Table 1. The samples were prepared by the high temperature vulcanization technique [19, 20] as used in [10] which has been shown to ensure

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completion of the crosslinking. One hundred parts of silicone rubber (PMV SiR) is mixed with thirty parts of fumed nano-silica (approx., 20nm diameter) by the double roll method, then ATH is added as required for a further fifteen minutes. ATH is a crystalline insulating material and though no direct measurement of its relative permittivity has been reported a value of 5.4 has been deduced from composites, which is greater than the value of 3.2 obtained for the unfilled rubber [1] and 3.6 obtained for the 20 % weight nano-silica rubber composite in [17]. A concentration of 10 phr was chosen for the ATH because its nano-composite has been shown to have the same tracking and erosion resistance as the usual commercial 100 phr micro-composite. A 10 phr micro-composite was also prepared for comparison purposes. The nano-ATH is spherical with a diameter of 20 nm and the micro-ATH has a mean diameter of 5 μm. Finally the crosslinking agent dicumyl peroxide (DCP) is added for a further five minutes followed by crosslinking and mould pressing at 5 MPa and 443 K for 10 minutes. The samples had a thickness of 1 mm and were cut into discs with a diameter of 70 mm. These were cleaned with ethyl alcohol and deionized water, and to avoid the adsorption of moisture, were kept in an oven at 363 K for 10 hours before the dielectric response measurement.

   The dispersion of nano silica, nano ATH and micro ATH in the samples is shown in Figure 1. Transmission Electron Microscopy (TEM) (HT7700) is used for the nano-particles and Scanning Electron Microscopy (SEM) (QUANTA 200 FEG) for the micro-particles. Each single particle of nano silica is about 20nm and, as reported in [15], can be expected to have an interphase layer of about 6 nm around it. Slight clustering giving a loose and polyporous aggregate ranging in size from several tens of nanometer to 100

nanometer was observed. The distribution of aggregates on a scale of 10 μm is not uniform but is similar to that shown for 50nm $BaTiO_3$ with 1-2 μm resolution in Figure 1 of [1]. The specific surface area of nano silica is about 200 mm^2/g obtained by BET (Brunauer-Emmett-Teller) specific surface area analyzer. The particle size of nano ATH is also several tens of nanometers, but the morphology of ATH clusters is more compact than those of nano-silica. The interphase thickness is not known in this case. In both the nano-silica and nano-ATH composites the distribution can be expected to be better in the 1mm thick samples used for measuring the dielectric response than found in the ultrathin samples used for the TEM measurement, however we expect the 1mm thick samples to be typical of the material when used commercially as macroscopic outdoor insulation.

Figures 1 (e) and 1 (f), show that micro ATH particles are irregular. The distribution of their diameters was obtained with a laser particle size analyzer (Mastersizer 2000), and it was found that more than 90% of the ATH particles had a diameter between 1 μm and 20 μm (about 4%, smaller than 1 μm) with an average diameter of 5 μm,

2.2. DIELECTRIC RESPONSE MEASUREMENTS

A Solartron 1255HF frequency response analyzer with a Solartron 1296 dielectric interface was used for the dielectric response measurements. Surface currents were avoided by using a three electrode (gold plated brass) system with a measurement electrode of 44 mm diameter and guard electrode of 50mm inner diameter and 60 mm outer diameter. This electrode system was used in [10] and the responses there indicated that a good contact was made. This was evidenced here by the absence of a loss peak process, which would arise from the charging of air gaps, in the response of the sample without any ATH in Figure2.

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The use of evaporated electrodes would prevent investigation via other techniques such as space charge measurements and can introduce new responses, see [21]. Before measurement the thickness of the sample was checked at five random places in the electrode area using a micrometer and found to vary no by no more than 2%. The sample was placed in a sealed metal test cell, which was kept in an oven with a Eurothern 2204 temperature controller that controlled the temperature fluctuation range to ±0.5 K throughout the duration of the measurement. The ac voltage was set as 2.0 V r.m.s, and measurements made between 10^{-4} to 10^{3} Hz for 7 points per decade, with the data acquired after two cycles of integration at each frequency. This allows the best characterization of the dielectric response consistent with the limitations of instrument error. Measurements were carried out at temperatures of 293, 313, 333 and 353 K, with a 7-hour delay before measurement at each temperature to guarantee that the sample was in a thermally stable state at that temperature. The compressive stress involved was insignificant compared to those in [2] and would not lead to any change in capacitance. In order to ensure that no physico-chemical changes had occurred during the time of measurement a preliminary check was made by immediately repeating the measurement at the highest temperature. No difference from the first measurement was observed.

3. RESULTS

3.1. DIELECTRIC RESPONSE

The frequency dependent complex capacitance of the different samples given in Figures 2 and 3 shows that introduction of micro-ATH filler into the nano-silica PMV SiR composite has introduced a very weak loss process around 10^{2} Hz (at T =353 K), and both

reduced the magnitude of the low frequency charge transport process (dominant below 10^{-1} Hz) and modified its frequency dependence. When the ATH is present as nano-particles the charge transport process is only slightly modified at T = 353 K, but the loss peak now becomes a prominent feature at the higher frequencies.

The dielectric response of higher concentration micro-ATH composites (80-120 parts ATH per 100 SiR) [10] is similar in form to that shown in Figure 2 for the lower concentration (10 parts ATH) micro-composite, consequently we will use the same equivalent circuit, Figure 4, to separate out the various contributions in the present case. These contributions are: an additive frequency-independent capacitance (C_∞) coming from responses occurring at frequencies higher than the measuring window [22], a DC conductance (G), a loss peak relaxation process, and a frequency dependent charge transport process termed a quasi-DC (Q-DC) mechanism [11]. The Q-DC process has been identified in a number of heterogeneous systems, (see [22-25]) and verified as a bulk process in [21, 26] and is due to the separation of opposite polarity charge pairs. At high frequencies the pairs are bound together in the form of a dipole over a local region termed a cluster. At low frequencies the pairs have sufficient time to separate from each other and transfer independently on structured fractal paths [27] between local clusters [11]. The Q-DC mechanism can thus be thought of as the dielectric response of a charge percolation system with concentrations below the percolation limit. It is therefore an appropriate form of response for the present system which is composed of filler particle clusters and has been used to interpret the behaviour of the micro-ATH filled silicone rubber [10]. The complex susceptibility corresponding to the Q-DC behaviour is given by [11];

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$$\chi^*(\omega) = \chi_0 \frac{\Gamma(1-p-n)}{\Gamma(1-n)\Gamma(1-p)} \left(1 + i\frac{\omega}{\omega_c}\right)^{n-1} \times \; {}_2F_1\left(1-n, 1+p; 2-n; \left(1 + i\frac{\omega}{\omega_c}\right)^{-1}\right) \quad (1)$$

Here $\Gamma(\text{-})$ is the gamma function and ${}_2F_1(\text{-},\text{-};\text{-};\text{-})$ is the Gaussian hypergeometric function. The Q-DC response is that of a percolation system at concentrations below the percolation limit, i.e. a connected path between the electrodes does not exist. However highly connected clusters exist within which opposite polarity charges can be separated. These function as dipoles with χ_0 denoting the net concentration of separated ion-pairs produced by a unit electric field. At frequency ω_c charge carriers start to move from one cluster to a neighbouring cluster and as the frequency reduces they transport independently through the more weakly connected percolation backbone, giving rise to charge separation over considerable distances with the number of connected paths reducing as the distance increases and the frequency decreases. In the limit of zero frequency and infinite separation the conductivity reduces to zero.

The low and high frequency limits are:

$$\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n-1} \quad \omega > \omega_c \quad \& \quad \chi'(\omega) \propto \chi''(\omega) \propto \omega^p \quad \omega < \omega_c \quad\quad (2)$$

with the exponents in the range $0 < n, p < 1$.

A number of empirical functions exist to characterise relaxation loss peaks (see [22]), however it is convenient to use the Dissado-Hill (DH) function [28] since this is determined by the way that dipoles or ion-pairs correlate their motions within local regions (clusters) and between regions without any charge transfer occurring between them. Such a physical picture would be appropriate to isolated regions of connected filler particles as well as molecular dipoles. The DH function incorporates the various empirical expressions as limiting cases depending upon the way the motions are correlated [29] and is given by:

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$$\chi^*(\omega) = \chi_0 \frac{\Gamma(1+m-n)}{\Gamma(2-n)\Gamma(m)} \left(1 + i\frac{\omega}{\omega_p}\right)^{n-1} \times \ _2F_1\left(1-n, 1-m; 2-n; \left(1 + i\frac{\omega}{\omega_p}\right)^{-1}\right) \quad (3)$$

Such that:

$$\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n-1} \quad \omega > \omega_p \quad \& \quad \chi'(0) - \chi'(\omega) \propto \chi''(\omega) \propto \omega^m \quad \omega < \omega_p \qquad (4)$$

Here χ_0 denotes the net concentration of dipoles or bonded ion-pairs produced by a unit electric field, ω_p is the characteristic relaxation frequency, and $0 < n, m < 1$.

An example of the fit to the measurements is shown in Figure 5, in which the contribution from each process is separately identified. The parameters derived for the measurement temperatures are given in Table 2, where the Q-DC and loss peak amplitudes have been converted from capacitance to relative susceptibility by multiplying by $d/(A\varepsilon_0)$, where d is the sample thickness, A is the electrode area, and ε_0 the permittivity of free space. It can be seen that the shape parameters of the loss peak (n, m) and the Q-DC (n, p) processes are essentially independent of temperature. The amplitude of the loss peak process is almost temperature independent, and though the variation in that of the Q-DC process is bigger there is no discernible trend with temperature. The value of C_∞ shows a steady but small decrease with increasing temperature. However Figure 3 shows that the whole response shows a substantial shift to higher frequencies as the temperature increases, therefore the frequencies, ω_p, and ω_c, and the conductance G must be strongly temperature dependent. Figure 6 gives an Arrhenius plot of these factors and it can be seen that the activation energy of all three is essentially the same at: 0.63 eV (ω_p), 0.62 eV (ω_c), and 0.62 eV (G).

4. DISCUSSION

4.1. COMPARISON OF NANO AND MICRO ATH COMPOSITES

The Q-DC process in the micro-ATH composites was assigned in [10] to the transport of ionic charges released by the ATH (i.e. Al^{3+}, and OH^-) around particle clusters (the high frequency C' $\propto$ C" $\propto$ ω^{n-1} response) and along restricted paths between ATH particle clusters (the low frequency C' $\propto$ C" $\propto$ ω^{-p} response). This is confirmed by the data presented in Figure 2 which shows that silicone rubber/nano-silica on its own exhibits a DC conductance characterised by C" $\propto$ ω^{-1} together with an additive Maxwell-Wagner-Sillars (MWS) process [30] charging a blocking capacitive region. In contrast the micro-ATH response in Figure 2 shows a low frequency Q-DC process in which C' $\propto$ C" $\propto$ ω^{-p} as observed in samples with higher ATH concentration [10]. The response of the $BaTiO_3$ nano-composite described in [1] exhibits a similar response to that of the micro-ATH composite which was assigned there to a DC conductivity in parallel with a bulk permittivity. Charging of the electrode was ruled out because there was no increase of the permittivity towards low frequencies. However the frequency range investigated in [1] was insufficient to obtain an unambiguous identification of the nature of the response. An increase in permittivity towards low frequencies due to a an electrode charging process would only be evident once the associated permittivity increased beyond the bulk value and could occur at much lower frequencies than those measured, as seen at 10^{-3} Hz for the no_ATH response in Figure 2. Since the frequency dependence of the loss tangent given in [1] is more consistent with a frequency dependent conductivity than a DC-conductivity a response such as the Q-DC behaviour identified here cannot be ruled out. An additional

feature of Figure 2 is that it shows that the loss peak process around 10^2 Hz originates with the presence of ATH filler and not the nano-silica SiR matrix on its own, a conclusion that could not be reached previously [10] because its weak strength led to it being almost obscured by the Q-DC response at the higher ATH concentrations.

The amplitude of the Q-DC process in the micro-ATH composites [10] was found to be thermally activated with activation energy 0.24 eV. This value was independent of the micro-ATH concentration and was taken to correspond to the energy required to release an ion from the body of the micro-particle to its surface where it is available to transfer from ATH-cluster to ATH-cluster. In the nano-composite the Q-DC amplitude ($\chi(0)$ in Table 2) does not exhibit a clear trend with temperature and is much smaller ($\sim 2.5 \times 10^{-3}$ to 5×10^{-3}) than for the micro-ATH composite (~ 1) which is independent of ATH concentration. This indicates that thermal promotion of ions from the body of the nano-ATH particles is not possible. Instead ions extracted in low concentration from nano-ATH particles into the interphase layer during manufacture of the composite are the only ones available to move around the nano-particle clusters and transfer between them in the Q-DC process.

In the micro-composite ion transfer between clusters ($\omega < \omega_c$) is activated with an energy reducing from 0.3 eV for a concentration of 80 parts of ATH to 0.25 eV for a concentration of 120 parts of ATH. This reduction was taken to be due to a decrease in the separation of neighbouring clusters of micro-particles as their concentration increased [10]. In the nano-composite the activation energy of ω_c is much higher (0.62 eV). This may be due in part to the larger separation between clusters arising from the lower ATH content (i.e. 10 parts as compared to 80 parts with activation energy of 0.3 eV). However it is also possible that the

modified structure of the silicone rubber matrix in the interphase zone [31] of the nano-particle makes it more difficult to move the ion between clusters.

In [10] it was suggested that the loss peak process was due to charging the surface of nano-silica clusters by ionic charge carriers originating with ATH particles in a MWS mechanism. In the micro-ATH composites studied in [10] the amplitude of the loss peak increased with temperature from $\sim$ 0.1 to 1. In the 10phr micro-ATH composite measured here the loss peak is almost completely obscured by the Q-DC process and its amplitude can only be roughly estimated as $\sim$ 0.01. In the nano-ATH composite the amplitude is about an order of magnitude larger and essentially independent of temperature at $\sim$ 0.1. This value is not too dissimilar to that found for the higher concentration micro-ATH composites of [10] and suggests that the same process may be taking place. The activation energy of the characteristic frequency ω_p for the micro-ATH composite could be only roughly estimated as $\sim$ 0.55 eV because the peak is nearly obscured by the Q-DC process, but the peak is well resolved in the nano-ATH composite and the activation energy of 0.63 eV is close to that of the micro-ATH composite. In the nano-ATH composite the activation energy for the loss peak frequency, ω_p, is the same as that of the DC and Q-DC charge transport processes, and thus it is likely that all three processes involve charge transport of ions through the silicone rubber matrix. In the Q-DC this would be required for the ions to transfer between the nano-clusters that are connected in the percolation backbone, and in the loss peak process for the ion transport to charge either nano-silica clusters or isolated groups of nano-ATH aggregates, or both. The characteristic frequency of the loss peak process in the nano-ATH composite is approximately 3 to 5 times greater than that of the Q-DC process (ω_c) unlike

in the micro-ATH materials [10]. It is therefore possible that the loss peak originates with some isolated groups of connected nano-ATH and nano-silica clusters for which the ionic charge carriers are unable to connect to the percolation backbone of the Q-DC system and thus their bound ion-pairs relax at the higher frequencies as a dipole for which $1/\omega_p$ is determined by the ratio of the capacitance of the group to the effective conductance that charges it.

The much higher activation energy for charge transport when micro-ATH is replaced by nano-ATH means it is more difficult for charges to displace in the nano-composite system. The temperature independence of the amplitude of relative susceptibility of the nano-ATH is also quite different to that of the micro-ATH composite where the release of charge carriers from the micro-ATH particle is thermally activated. These results indicate that if micro-ATH were replaced by nano-ATH the dielectric losses over the measured frequency range would be reduced at temperatures below 353 K, which would be beneficial for outdoor applications. Furthermore the lower ac transport currents would inhibit the build-up of high internal fields by charge displacement induced by surface charging of the nano-ATH composite in comparison with the micro-ATH composite, and thereby favour a longer their service life.

4.2. CARRIER TRANSPORT DISTANCE

The Q-DC process is produced by the freeing of ionic charge carriers from particle clusters and their long range transport within the composite. By assuming that it is produced by charge carriers performing a random walk in a percolation system estimates can be obtained for the shortest displacement within a particle cluster and for the longest

transport distance between clusters i.e. on the fractal paths of the percolation backbone [32 -34].

Defining the walk dimension [33] to be d_w the distance R that carriers displace in a time t (proportional to the number of steps taken) corresponding to a frequency ω is:

$$\omega \propto t^{-1} \propto R^{-d_w} \tag{5}$$

The frequency power law exponents (n in the high frequency branch of the Q-DC and p in the low frequency branch are determined by the ratio of d_w to the fractal dimension d_f of the structure upon which the walk takes place [27, 32];

$$n = 1 - d_f/d_w \equiv 1\text{-}p \tag{6}$$

The susceptibility magnitude at frequency ω is thus related to the walk distance R through;

$$\chi'(R) \propto R^{d_f} \tag{7}$$

The normal diffusion limit corresponds to $d_w = 2$ and $n = 0.5$.

In the high frequency branch of the Q-DC n > 0.5 and since in order to have a connected path $d_f \geq 1$ a lower bound can be estimated for d_w using the experimental value of n and d_f =1. Table 2 gives the average value of n for the Q-DC as 0.705 and hence the lower bound for d_w is 3.39. Since $d_f \leq 3$ the upper bound for d_w is 10.2, i.e.

$$3.39 \leq d_w \leq 10.2 \tag{8}$$

In this range $d_w > d_f$ and the exploration of the cluster is compact , i.e. charge separation by a distance R requires many more steps than would be the case along a straight linear path. The frequency where the high frequency branch of the Q-DC crosses over to the low frequency branch can be taken to correspond to a charge displacement across the diameter of the ATH agglomerates shown in Figure 1c & 1d; at higher frequencies the charge

separation remains within the agglomerate and at lower frequencies charges transfer between agglomerates. This gives a separation of $R_c \sim 100$ nm at $\omega = \omega_c = 6.67 \ 10^{-1}$ rad/s when T = 293 K. Therefore the charge separation (R_{min}) at the highest frequency for which we have identifiable Q-DC data at this temperature, i.e. $2\pi 10^2$ rad/s is given by:

$$0.5 \text{ nm} < R_{min} < 13.5 \text{ nm} \tag{9}$$

This corresponds to positive and negative charge separation either around the surface of single nano-ATH particles in the agglomerate cluster or between neighbouring particles in the cluster, and is consistent with the Q-DC cluster model. The ω^{n-1} branch of the Q-DC will end at a frequency high enough that ionic charge separation is impossible [32, 34].

A similar calculation for the low frequency branch of the Q-DC process leads to:

$$1.7 < d_w < 5.09 \tag{10}$$

The longest range over which the Q-DC transport is observed to occur is at 353 K which has the largest frequency range over which the low frequency branch is observed. This gives the bounds for the largest observed transport range R_{max} as:

$$0.9 \ \mu m < R_{max} < 72 \ \mu m \tag{11}$$

The ω^p response is still ongoing at the lowest frequency measured and can continue down to the frequency corresponding to the longest connected fractal path, i.e. largest percolation backbone [32, 34] or the sample thickness [35].

These estimates show that charge carriers bound together as dipoles on a nano-ATH cluster explore the ATH particle surfaces and transfer to neighbouring particles in an agglomerate in a compact way such that many steps and a long time are required before they can separate across the agglomerate and transfer to other clusters. Once they have enough time

to transfer between clusters the exploration becomes less compact and they can separate over distances of hundreds of microns within the materials if sufficient time is allowed.

5. CONCLUSIONS

The dielectric response of nano ATH filled silicone rubber and silica based composites have been investigated and decomposed into different kinds of dielectric processes that have been described using the Dissado-Hill cluster model. In the frequency window and temperature range used in this study, two kinds of dispersion processes were observed: a Q-DC process and a loss peak process. A comparison with silicone rubber/nano-silica that did not contain ATH established that the Q-DC and loss peak process are caused by the charge carriers Al^{3+} and OH^- that can be released from the ATH particles.

The amplitude of the Q-DC transport process was found to be much smaller than the corresponding process observed in the micro-ATH composite. The loss peak process in the nano-composite was clearly resolved unlike that in the micro-composite and had a much larger amplitude. In the case of nano-ATH, the activation energies of all processes were found to be the same and much bigger than the corresponding value found for the Q-DC process observed in the micro-ATH composite. It was found that the concentration of ions that can be released for the Q-DC charge transport by the nano-ATH was much less than that released by micro-ATH. Estimates of the range of charge separation occurring in the Q-DC process showed that at frequencies greater than the characteristic frequencies the carriers moved around the surfaces of nano-particles in an agglomerate, while at lower frequencies the separation extended to distances of the order of tens to hundreds of micrometres.

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Figure 1. (a,b) TEM of nano-SiO_2 (c,d) TEM of nano-ATH, (e,f) SEM of micro ATH

Figure 2. Complex capacitance of silicone rubber – Comparison of silica based composites without ATH (no_ATH) and with micro ATH (μm_ATH) at 353 K.

Figure 3. Complex capacitance of silicone rubber – silica based composites with nano ATH (nm_ATH): C' (solid markers) and C'' (open markers), 293 K (green triangles), 313 K (blue pentagons), 333 K (pink diamonds), 353 K (red circles)

Figure 4. Equivalent circuit for silicone rubber composites

Figure 5. Equivalent circuit fitting of the complex capacitance for nm_ATH at 353 K. The open markers denote the original experimental data and the color lines denote contribution of the different dielectric process. The black lines are the Least Square fit to the results of the real and imaginary parts of the complex capacitance containing all the processes

Figure 6. Arrhenius plot of ω_p Loss peak process, ω_c Q-DC and DC conductance.

Table 1. Details of silicone rubber composites. The numbers refer to composition by relative weight

Composition	no_ATH	μm_ATH	nm_ATH

PMV SiR	100	100	100
SiO_2	30	30	30
micro ATH	0	10	-
nano ATH	0	-	10

Table 2. Equivalent circuit fitting results at different temperatures

Parameters	353 K	333 K	313 K	293 K
Loss Peak				
$\chi(0)$	1.25×10^{-1}	1.25×10^{-1}	1.19×10^{-1}	1.43×10^{-1}
ω_p (rad/s)	2.29×10^{2}	3.86×10^{1}	1.18×10^{1}	2.99×10^{0}
m	0.60	0.61	0.53	0.61
n	0.74	0.75	0.74	0.74
Q-DC				
$\chi(0)$	4.87×10^{-3}	2.68×10^{-3}	2.42×10^{-3}	4.36×10^{-3}
ω_c (rad/s)	4.50×10^{1}	1.35×10^{1}	3.60×10^{0}	6.67×10^{-1}
p	0.59	0.59	0.59	0.59
n	0.72	0.68	0.72	0.70
G (pS)	9.23×10^{-2}	2.75×10^{-2}	7.92×10^{-3}	1.39×10^{-3}
C_∞ (pF)	38.37	39.67	41.26	42.77