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Performance of HTV Silicone Rubber under Artificial AC and DC Corona/Ozone Test

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Abstract: This paper concentrates on presenting the changes of properties of high temperature vulcanized (HTV) silicone rubbers when exposed to 100 hours long corona/ozone treatment in a multi-needle electrode system, as suggested by CIGRE Working Group D1.14 and in detail reported in our former publication. The material samples were treated by either AC or DC corona sources. The HTV samples used in this test contained one type of a commercial HTV silicone rubber (including both post- and unpostcured specimens) based on polydimethylsiloxane (PDMS) as well as model HTV silicone rubbers containing increased amount of methylvinylsiloxane (MVS) and filled with aluminum-trihydrate (ATH) of different proportions. Material characterization methods involving volume and surface resistivity measurements, dielectric response (DR) measurement, as well as tensile tests were adopted to trace the performance changes of the samples induced by the AC or DC corona treatments.

1 INTRODUCTION

To secure the long-term reliable performance of composite insulators in high voltage outdoor environments, one of the main challenges that polymeric insulator manufacturers, utilities and researchers have long been encountering for is to make known the material interaction with various types of electric discharges. Therefore, the resistance to corona as well as its byproduct ozone is among the vital parameters to be evaluated, as recognized by CIGRE WG D1.14 [1]. The testing procedure itself, the evaluation methodology as well as the determination of the threshold parameter values (minimum requirements) are of significance when it comes to eventual standardization of the elaborated artificial corona/ozone test.

Poorly designed or degraded insulator hardware (including corona rings) as well as presence of water droplets on insulator housing surface are the two main sources of corona discharges that act on the polymeric insulator surface. On the other hand, from an investigation point of view, an artificial corona ageing tests has to be developed so as to avoid the randomness of distribution and uncontrollability of the discharge intensity. For this purpose, different corona/ageing tests have been designed [2-11] for investigating the impact of long-term corona discharges on the hydrophobicity characteristics of composite insulator surface as well as on the degradation mechanisms involved. Most of the attempts carried our internationally have so far concentrated on studying the effects of AC corona, a logical consequence of the domination of AC based transmission in the world's electric power systems. However, DC based transmission and distribution of electric power is nowadays an alternative solution for building new power system links and for replacing the old and ageing infrastructure. Thus more attention needs to be paid to the effects of DC corona on polymeric materials.

This paper presents a comparison of degradation effects imposed by AC and DC coronas on two types of silicone rubber materials, a commercial HTV rubber and a model HTV rubber containing different proportions of ATH filler. To trace and evaluate the changes induced by the corona/ozone ageing tests, dielectric and mechanical properties were measured and analyzed.

2 EXPERIMENTAL

2.1 Corona ageing test setup

The original version of the test arrangement for AC corona treatment, including detail description of the electric circuit, is described in [12]. For obtaining a homogeneous distribution of electric field in the vicinity of the treated sample [13], the distance between the tip of the outermost needle and the sample surface of the sample investigated has been set at 40 mm. Meanwhile, a mechanical pre-stressing is also imposed on the treated elastomeric material (3 % elongation). For the the DC corona treatment, a single phase half cycle diode rectifier is connected to the output of the step-up transformer. For filtering purposes, a 45 nF smoothing capacitor bank is also included in the rectifier circuit. For comparing the influences of the 100 h long AC and DC corona treatments, voltages of ± 28 kV DC, which are the peak values of the applied sinusoidal 20 kV AC voltage, were utilized.

2.2 Samples and testing procedure

Two types of HTV silicone rubber samples were used in this study. The first type was HTV silicone rubber, Elastosil R401/60 from Wacker Silicones (ρ = 1.14 g cm^{-3}), based on PDMS and a reinforcing silica filler. It was crosslinked with 0.7 wt. % dicumylperoxide (dispersed in 0.7 wt. silicone oil). Samples of this material were further divided into two test batches; the first batch consisted of samples crosslinked at 165 ℃/ 100 bar (10 MPa) for 15 min and then postcured at 170 ℃/ 4 h in a hot oven. The second batch was crosslinked at 165 ℃/100 bar (10 MPa) for 15 min only, meaning that the samples still contained some residuals from the crosslinking process. This way of selecting materials for the studies aimed at figuring out if the crosslinking by-products could play any role in the corona damage mechanism. The second type of test object consisted of three model HTV silicone rubbers containing increased amount of methylvinylsiloxane (MVS) filled with silanized ATH and reinforcing silica filler. The mass ratio of MVS/ATH/silica for the three formulations was 5:4:2, 5:5:2, as well as 5:6:2, which thereafter are referred to as HTV-4, HTV-5, and HTV-6, respectively. The model HTV samples used in this work were crosslinked at 165 ℃/100 bar (10 MPa) for15 min and then postcured at 70 ℃/168 h in a hot oven.

The dimensions of all the rubber samples put into the treatment vessel were ~100 x 100 x 2 mm^3, while the corona discharge activity affected their central circular part of approximately 90 mm in diameter. Before the treatments, all the prepared samples were cleaned with propanol and then left in air until drying out for at least 3 hours. Three samples of each material were treated one after another, by AC and DC (positive and negative polarities) coronas for 100 h. Measurements of dielectric parameters, such as volume and surface resistivities and dielectric spectroscopy in the frequency domain, were conducted prior and after the corona treatments for each of them. Thereafter, the treated samples were punched into 6 dumbbell-shaped samples for performing mechanical testing (tensile strength and elongation at break). Additionally, virgin reference samples were characterized according to the same procedure.

3 RESULTS AND DISCUSSIONS

3.1 Corona discharge intensity

Corona discharge intensities for different corona types, i.e. AC or DC, were characterized by measurements of the released power from the multi-needle electrode, while with the investigated sample was mounted underneath. At the selected treatment levels (AC 20 kVrms as well as DC 28 kV), the discharge intensities were observed to be dependent on the type of material under test. For Elastosil samples in case of either AC or DC corona exposures, see Figure 1(a), the released power for the postcured samples was relatively higher than for the unpostcured samples. However, the power released under negative DC corona was higher than that the one of positive polarity; for the postcured samples, the value measured at negative polarity was even close to that from AC corona (~1.8 W), up to ~1.6 W at the treatment level. For the unpostcured Elastosil samples, the power released from the electrode was approximately 1.5 W, 0.9 W and 1.1 W for AC, DC positive and DC negative discharges, respectively. On top of these, for the model HTV samples, the released power also followed the similar regularity, however, the differences were less pronounced. Moreover, no obvious influences of these three material formulations upon the corona power could be observed. One plausible reason for the relatively higher released power during AC corona discharge is that the DC discharge activity was impeded in the test arrangement by electrostatic charging of the treated sample surface, which in turn modified the electric field distribution in the discharge region.

3.2 Ozone concentration

The results of the ozone concentration measurements during the corona treatments are summarized in Figure 2. For Elastosil samples, the concentrations of ozone during DC corona exposure were found to be significantly lower than that of AC case. For the model HTV samples, however, the ozone concentrations monitored for all the samples investigated were practically at the same level. Reasons for the observed differences are so far not clear. However, we suspect that crosslinking residues as well as the significantly lower sample resistivity may play here a role. The model HTV samples were postcured in a thermal chamber for a much longer time as compared to Elastosil samples and the ozone concentration levels during the AC corona treatment seemed depending on its length; the longer post-curing time the ozone concentration became lower.

As shown in paper [12], for a specific polymeric specimen, the ozone concentration during AC corona treatments is proportional to the power released from the corona source. This correlation is however no longer valid when compared with DC corona cases. As revealed earlier, for the postcured Elastosil samples the corona power measured during the AC discharge was comparable with that for negative DC one, while at the same time the measured for these two cases ozone concentrations were remarkably different. This may indicate that the generation mechanism of ozone during AC corona exposure differs from that during DC one. It additionally was observed during DC corona exposures that with similar released power, for instance as comparing postcured Elastosil with HTV-5, the monitored ozone concentration were also significantly different. It is hence believed that the behavior of accumulated surface charges on the treated polymeric samples, which is closely related to the material's dielectric parameters, may be responsible for this effect.

3.3 Dielectric properties

The dynamic behavior of the electric polarization and conduction after the corona treatments were investigated by carrying out the measurements of bulk and surface charging currents in ambient atmosphere (at room temperature 22±3 °C and relative humidity 30±5 %) twice, first immediately after the treatment and thereafter two weeks later. Resulting observations are summarized in Figure 3 for the postcured Elastosil material. For the first round of the measurements, both volume and surface charging currents increased after AC or DC corona treatments. The changes observed on the surface were however stronger responsive to the treatment. At the same time, the effects of AC corona treatments were more pronounced than the DC ones, for both the volume and the surface charging currents. However, two weeks after treatment, the surface charging currents for the DC corona treated samples recovered to the initial state, while for the AC corona treated sample the recovery was incomplete. This effect can be associated with observed changes of surface hydrophobicity, as it recovered much slower for the samples treated by AC corona than for the DC treated samples. Meanwhile, the volume charging currents remained unchanged with storage time. One possible explanation of the surface current recovery behavior is that the resting allowed low molecular weight (LWM) silicone derivatives diffusing to the surface and shielding the hydrophilic OH groups generated during the

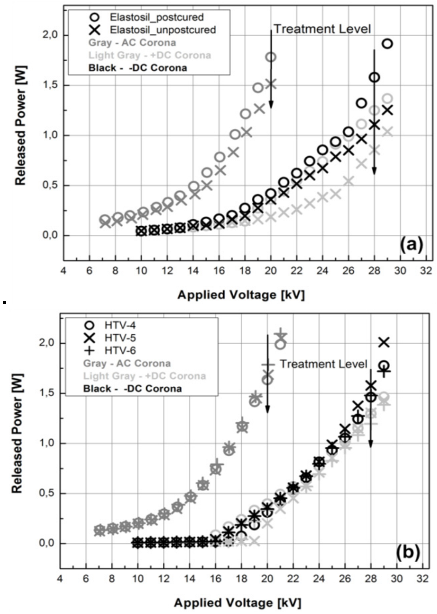

Figure 1: Comparisons of released power from the multi-needle electrode, initiated by AC and DC corona discharges, as measured for Elastosil (a) as well as for the model HTV samples (b).

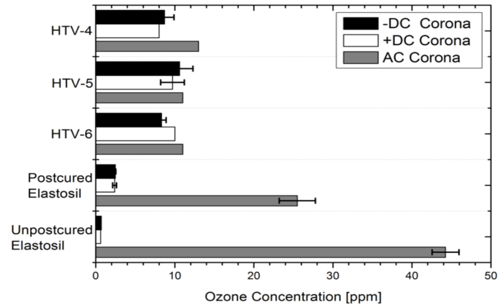

Figure 2: Ozone concentration measured during the AC and DC treatments of polymeric samples investigated.

corona treatments. On the other hand, for the AC corona treated sample, due to a more severe surface oxidation resulting from higher ozone concentration present during the treatment, diffusion of LMW silicone derivatives to the material surface could not equally efficiently influence the surface dielectric properties, as it did on the DC corona treated surfaces.

The results summarized in Table 1 show that the treatments by all types of corona have influenced the levels of both volume and surface resistivities. It is important to note that the volume resistivity of the model HTV materials is lower than that of Elastosil and it can be attributed to a difference in filler content. The arrows in the columns "Effect of treatment" indicate the trends in logarithmic scale as compared with initial reference values First of all, when comparing the postcured with unpostcured

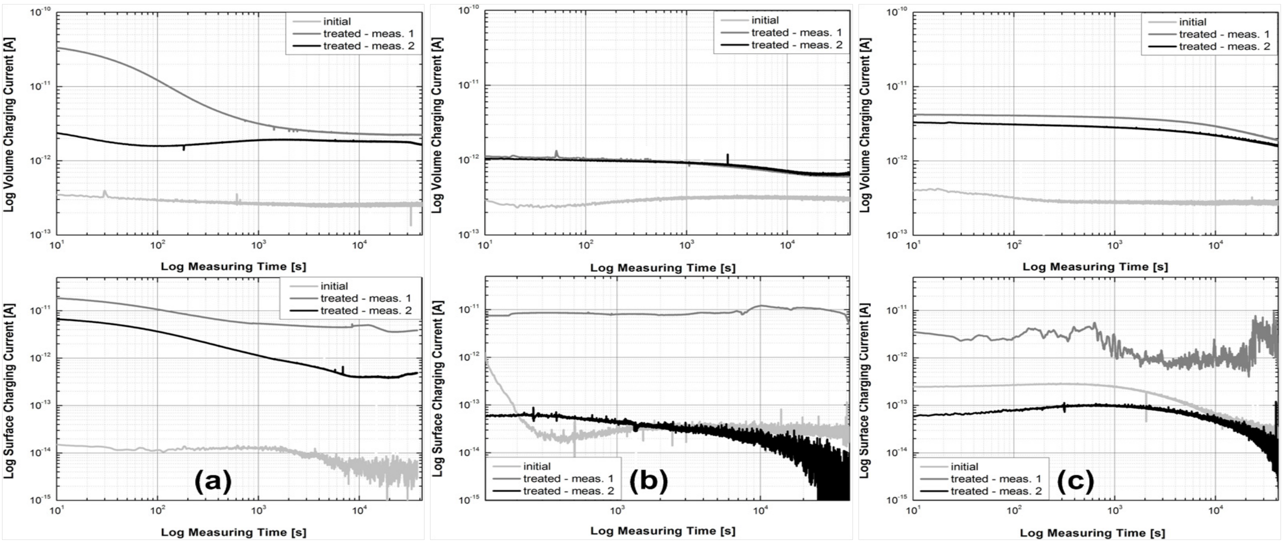

Figure 3: Volume (top) and surface (below) charging currents for postcured Elastosil samples treated by AC corona (a), positive DC corona (b) and negative DC corona (c). Measurements performed directly after an end of corona exposure ('treated – meas. 1') as well as two weeks after end of exposure ('treated – meas. 2').

Elastosil samples, for each specific type of corona exposure as regards either volume or surface resistivity, the postcured Elastosil samples exhibited more susceptibility to the corona treatments that also agrees with the measurement results on corona power (se section 3.1). It can be observed that for surface and volume resistivities of Elastosil samples, more pronounced influences were imposed by AC corona due to the higher discharge intensity. One exception is that the influence of negative DC corona on the volume resistivity reached a comparable level to the AC case for postcured Elastosil, i.e. a reduction by 0.94 decade. Such a degree of reduction is in line with the measured similar levels of corona power released under negative DC and AC coronas.

Although the more pronounced effects of each specific type of corona treatment were imposed on surface resistivity of Elastosil samples, it was however not the case for the model HTV samples. The latter follow this regularity in the case of AC corona exposure only. Furthermore, the volume resistivities for all the formulations of the model HTV samples increased as compared with the initial references with no substantial difference regarding the effect of the formulation. Since the model HTV samples contain increased amount of methylvinylsiloxane, the vinyl groups are expected to yield a more complete crosslinking of the polymer during the manufacturing process as well as increased sensitivity towards oxidative crosslinking during corona exposures.

The results of the dielectric response measurements for the postcured Elastosil as well as for model HTV samples prior to and after the corona treatments are illustrated in Figure 4 and Figure 5. For the postcured Elastosil samples, the spectra in the low frequency region (below 10-2 Hz for the initial state and after the AC corona treatment as well as below 10-1 Hz for the samples treated by DC corona) a typical DC conduction behavior can be seen, while no significant variations can be found in the real part of permittivity. The imaginary permittivity however showed obvious trend to increase after the corona treatments; most significantly in the sample treated by AC corona, followed by the one treated by negative DC corona and finally the one treated by positive DC corona – the same ranking sequence as regards the corona power released from the multi-needle electrode.

On the contrary, the dielectric response in frequency domain for the model HTV samples behaved differently as exemplified in Figure 5 for HTV-5 material. The spectra in the low frequency region indicate that the low frequency dispersion polarization dominates the response. However, both the real and imaginary part of permittivity decreased after the corona treatments as compared to the initial state while no substantial differences could be observed between the different corona types.

3.4 Mechanical properties

Since polymeric housing materials are expected to retain mechanical integrity under the influence of corona/ozone exposure, the purpose of this investigation was to assess the changes of tensile strength and elongation at break imposed by the corona exposure. For obtaining statistically significant results, 6 specimens were cut out of

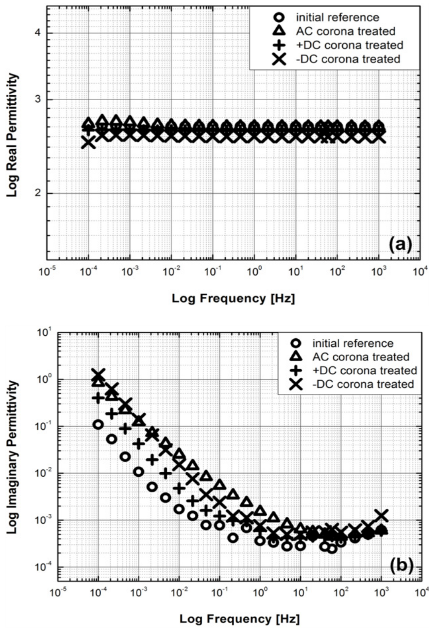

Figure 4: Real (a) and imaginary (b) parts of complex permittivity for postcured Elastosil samples treated by AC and DC coronas.

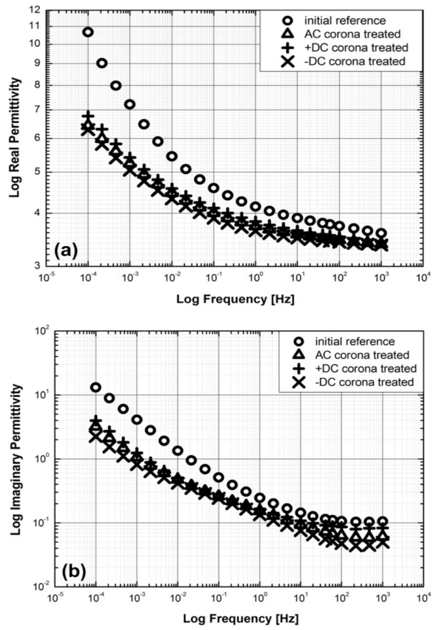

Figure 5: Real (a) and imaginary (b) parts of complex permittivity for HTV-5 treated by AC and DC coronas.

Table 1: Values of volume and surface resistivities of Elastosil as well as the model HTV samples treated by AC and DC corona, measured directly after the 100 h lasting corona treatments and calculated for the time of current measurements equal to 3.6 x 104 s.

Batches		**Volume resistivity (Ωm)**		**Effect of treatment (decades)**	**Surface resistivity (Ω/sq)**		**Effect of treatment (decades)**
		Initial	**Treated**		**Initial**	**Treated**	
Unpost. Elastosil	**AC_{rms}**	8.49×10^{14}	4.44×10^{14}	↓ **0.40**	2.15×10^{18}	1.94×10^{16}	↓ **2.02**
	+DC	1.04×10^{15}	1.09×10^{15}	↓ **0.01**	1.07×10^{18}	4.51×10^{17}	↓ **0.66**
	-DC	9.48×10^{14}	8.11×10^{14}	↓ **0.14**	7.56×10^{17}	7.10×10^{17}	↓ **0.05**
Postcured Elastosil	**AC_{rms}**	1.67×10^{15}	1.93×10^{14}	↓ **0.97**	7.45×10^{18}	5.55×10^{15}	↓ **3.19**
	+DC	1.50×10^{15}	7.28×10^{14}	↓ **0.42**	7.26×10^{17}	1.77×10^{15}	↓ **2.54**
	-DC	1.69×10^{15}	2.31×10^{14}	↓ **0.94**	8.29×10^{17}	1.26×10^{16}	↓ **1.70**
HTV-4	**AC_{rms}**	1.94×10^{13}	4.45×10^{13}	↑ **0.36**	3.05×10^{16}	1.05×10^{15}	↓ **1.46**
	+DC	3.84×10^{13}	6.56×10^{13}	↑ **0.23**	7.94×10^{16}	2.84×10^{16}	↓ **0.44**
	-DC	5.92×10^{13}	7.87×10^{13}	↑ **0.12**	8.08×10^{16}	7.99×10^{16}	↓ **0.004**
HTV-5	**AC_{rms}**	2.24×10^{13}	1.19×10^{14}	↑ **0.73**	4.13×10^{16}	3.99×10^{14}	↓ **2.01**
	+DC	1.97×10^{13}	1.16×10^{14}	↑ **0.77**	4.68×10^{16}	4.36×10^{16}	↓ **0.03**
	-DC	2.02×10^{13}	2.53×10^{14}	↑ **1.10**	1.35×10^{17}	6.84×10^{16}	↓ **0.29**
HTV-6	**AC_{rms}**	9.21×10^{12}	2.51×10^{13}	↑ **0.43**	1.78×10^{16}	1.25×10^{15}	↓ **1.15**
	+DC	4.71×10^{12}	3.45×10^{13}	↑ **0.86**	1.67×10^{16}	1.41×10^{16}	↓ **0.07**
	-DC	1.54×10^{13}	3.64×10^{13}	↑ **0.37**	2.55×10^{16}	2.43×10^{16}	↓ **0.02**

each treated sample. The results are shown in Figure 6. For Elastosil the samples were cut in parallel and perpendicular to the pre-stressing direction during the treatment (dash lines refer to the parallel direction while the solid lines to the perpendicular one). As shown in Figure 6, for both the mechanical parameters investigated, more pronounced effects were indeed found for the model HTV samples, with reductions up to 15.5 % in tensile strength and up to 26.4 % of elongation at break. This indicates an occurrence of apparent bulk degradation. For Elastosil, on the other hand, only a slight reduction of the mechanical strength could be noticed. This indicates that Elastosil

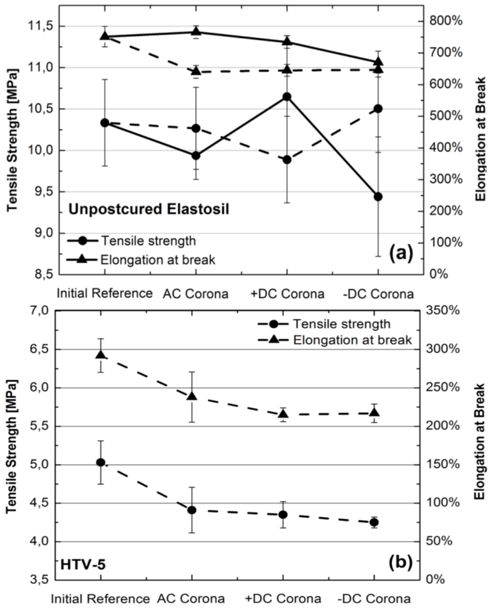

Figure 6: Tensile strength as well as elongation at break for the unpostcured Elastosil (a) and the model HTV-5 samples (b).

samples are more resistant to degradation of mechanical properties during the corona treatments.

4 CONCLUSIONS

The performed investigations reported in this paper describe the changes of dielectric and mechanical properties of two types of silicone rubber based materials under an exposure to deterioration tests applying AC and DC corona treatment of material sample surfaces. The results aiming at characterizing these corona sources showed that both the corona discharge intensities as well as the concentration of ozone generated by the discharges were dependent on the dielectric parameter of the materials treated. For Elastosil samples, the corona treatments yielded increase of dielectric losses and reduction of bulk and surface resistivities. The degree of these changes could be correlated with the level of power released by the discharge activity. However, no considerable reduction of mechanical properties in terms of tensile strength as well as elongation at break was observed.

For the other type of the tested material, namely the model HTV silicone rubbers containing increased amount of methylvinylsiloxane (MVS) and filled with different amounts of aluminum-trihydrate (ATH), an increase in bulk resistivity as well as reduction of dielectric permittivity and losses were observed. Such a result may be attributed to a possible influence of vinyl groups, providing additional crosslinking and therefore influencing the content of polar residues that modify the dielectric response. The changes of mechanical properties of the model HTV materials appeared to be relatively strong as compared with the performance of Elastosil samples.

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