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Chapter 1

Nanocomposite for Space Charge Suppression in HVDC Cable Accessory

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Abstract

HVDC cable accessories made of ethylene-vinyl acetate copolymer (EVA) by incorporation of specific fillers have to face the problem of space charge accumulation. The effects of doping contents on the space charge behaviors of EVA/ZnO composite are not completely clear. EVA composites are prepared with the fraction of 0, 1, 5 and 10 wt%, respectively, with which 5 wt% nano-sized plus 5 wt% micro-sized ZnO-doped samples are chosen for comparison. Obtained results show that the particles in EVA composite are in homodisperse. The permittivity is increased by ZnO doping and the dissipation factor of EVA composites with 1 and 5 wt% nanoparticles is lower at the lower frequencies. The homocharge injection occurs in cathode instead of anode when ZnO nanoparticles are introduced and 5 wt% nanoparticle doping performs well in suppressing space charge injection. The electric field in the 5 wt% nanoparticle-doped EVA distributes more uniformly under the high electric stress than that of others. During the depolarization procedure, the total remnant charges of 10 wt% doped samples are the least in the final. The above results are well explained by the DC conduction, apparent mobility and trap distribution characteristics.

Keywords: HVDC, cable accessory, space charge, ZnO nanoparticle, trap distribution, carrier mobility

1. Introduction

The features of the transmission capability and the material are combined by the polymer insulated HVDC cables for high-power, long-distance underwater or underground transmission,
so they have many advantages [1–4]. Space charge can be accumulated under DC electric stress within the insulation matrix through charge injection from impurities’ electro-dissociation and electrodes [5]. The electrical field in cable insulation may be changed seriously because of the accumulation of space charge, particularly after polarity reversal which causes probably premature failure and material degradation [6, 7].

Especially being a vital part of the HVDC networks, the performance of cable accessories is critical to the system’s reliability considering the mechanical, thermal and electrical characteristics of the models which are combined with great dangers with install faults and environmental pollution [8–10]. Given the complicated geometry, particular fillers’ doping and the interfaces’ existence between the accessories insulation and the cable insulation, the accumulation of the space charge as well as its influence has become much harder to make predictions [11].

People use EVA composites very often within the cable accessories because of the manufacture of cable accessory insulation, semi-conductive insulation jackets as well as heat shrinkable insulation and it is able to sustain higher filling contents with no yielding to the mechanical strength loss nor embrittlement and can be cross-linked in an easy way [12, 13]. The use of nonlinear resistive fillers as well as particular conductive additives and so on can create cable accessories which are from EVA composites, for the uniform electric field [14]. At the same time, the cable accessories which are created by EVA also needed to deal with the issue of the accumulation of space charge.

It has been proved that nano-sized particles are a useful strategy of suppressing the accumulation of space charges in dielectrics. A lot of reports have shown that the space charges are suppressed by the interfaces between the polymer matrix and the additives. Fabiani et al. argued that the use of larger TiO$_2$ nanoparticles to detect conductive processes in EVA nanocomposites has less accumulation of space charges, lower activation energy and lower conductivity [15]. Delpino et al. put forward the outcomes of conduction current measurements and space charges of 5 wt% EVA/montmorillonite nanoplayer composite and discovered big conduction current magnitude and space charge [16]. Montanari et al. did some researches on the electrical properties of layered micron and nano-sized silicate-filled EVA copolymers, and improved the space charge accumulation behavior by changing the nanofillers [17]. However, few studies have helped to know EVA’s space charge dynamic actions full of ZnO under the DC electrical stress.

The paper aims at revealing ZnO doping’s influence on the actions of space charges, electric field distribution as well as dielectric properties within EVA composites. According to the outcomes, an important influence on the dielectric properties and DC conduction exists in ZnO introduction. Homocharges accumulate near the negative electrode after introducing ZnO nanoparticles and 5 wt% concentration shows better suppression of space charge injection. The distribution of the electric field is more uniform in the 5 wt% doped EVA. The chains can be damaged by the extra micro-sized particles and brand-new disadvantages may be created as well, which may act as carriers.
2. Experiments

2.1. Specimens

There is a density of 0.93 g/cm$^3$ and 14% vinyl acetate content in the EVA 1045. ZnO particles' grain sizes are ~2 μm and ~40 nm. The ZnO had been dried for over 24 h within a desiccator prior to dispersion in the EVA. The mixing was performed at 90°C for 15 min by a two-roll mill set at 30 rpm rotor speed and 2 mm nip gap. All the compounds had been cured for about 5 min at 120°C in a press that was heated electrically under the pressure of 10 MPa and chilled down in a natural way to the room temperature. Specimens that had ~500 μm thickness had been prepared through the incorporation of ZnO nanoparticles to EVA matrix with 10, 5, 1 and 0 wt% fraction respectively, where 5 wt% micro-sized and 5 wt% nano-sized ZnO filled EVA specimen had been set as contrast. ZnO's dispersion in the EVA matrix had been explored through scanning energy dispersive spectrum analysis (EDS) and electron microscopy (SEM) with Hitachi S4800. The mixed doping composites as well as 5 wt% nano ZnO doped EVA’s SEM photograph can be seen in Figure 1. The white spots are the nano fillers in Figure 1a. No important aggregation can be seen in the specimens and the nano fillers are dispersed in a uniform way. The bigger particle stands for the micro-sized ZnO in Figure 1b. Figure 2 is EDS’s from Figure 1 and the zinc factor’s higher contents are introduced because of more ZnO doping. The fillers’ uniform dispersion may be helpful for analyzing the space charge properties as well as the mechanism for dielectric.

Figure 1. Distribution of ZnO particles in EVA composite.
2.2. Test procedure

2.2.1. Space charge measurements

The PEA strategy had been adopted to study the space charge characteristics in ZnO/EVA composites. The width of 10 ns as well as the pulse voltage with 500 V amplitudes had been adopted and silicone oil had been adopted for ensuring great acoustic contact between the electrodes and the specimen. The materials had been dealt with by the Lab VIEW software through the use of a deconvolution technique and a calibration. The specimen has a diameter of about 40 mm and a thickness of 500 μm. The temperature was set as 40°C and the electrical field was set averagely as 25 MV/m. Space charge profiles had been recorded along the depolarization and polarization process every 5 s.

2.2.2. Dielectric properties and DC conduction current measuring

The ZnO/EVA composites’ dielectric properties had been measured in the paper through Novocontrol Concept 40. An electrometer (Keithley 6517B) had been used to measure the conduction currents with the space charge measurements under the same condition. Every specimen had been held between electrodes before the measurements for more than 12 h for the purpose of dissipating excess charges. The existing values had been recorded in the stressing process every 2 s.

3. Effects of ZnO contents

3.1. Specimen characteristics

The relation among the frequency, dissipation element and the relative permittivity of the EVA/ZnO composites is presented in Figures 3 and 4. As the ZnO concentration varies from 0 to 10wt %, relative permittivity improves from 2.59 to 2.92. While it comes to 3.0 for the hybrid doping. The dissipation factor has been greatly improving over a majority of the frequency range for the doped specimens, but an opposite trend is shown by the undoped specimen. The 5 and 1 wt% filled specimen’s loss factor is lower at the lower frequencies compared with that.
of the undoped one. The dissipation element is bigger for the higher frequency range or the higher doping proportion.

The relaxation mechanisms and the dielectric polarization determine the dielectric properties in the nanocomposites to a great extent [18]. The polarization which connects with the permittivity happens in the matrix-filler interfaces and the EVA, ZnO particles. In terms of the base EVA, the mobility of the long molecular chain makes contributions to the polarization process. Therefore, the relative permittivity is not high. Because there is relatively higher permittivity in the inorganic ZnO particles, the fillers are helpful to improve the EVA composites’ permittivity with higher fillgrade. Nevertheless, the polarization is not improved so much as expected with less content of particles. The possible cause is that the matrix-filler interfaces are introduced by the nanoparticles doping, which may impose restrictions to the polymer polarization and cause the slow improvement of permittivity (Figures 3 and 4).

3.2. Space charge accumulation

Figure 5 presents ZnO/EVA composites’ space charge polarization under \(-25 \text{ kV/mm}\) on average. The homocharges within the pure EVA comes from the positive electrode with the application of the stress. The charge packages consisting of holes continued to move toward the negative electrode with the increase of time under the electric stress. There was no clear charge injection in EVA near the negative electrode. Figure 5b shows that the homocharges injected from negative electrode, which is opposite to the pure specimens. It’s noticeable that good performance is demonstrated by the EVA composites doped with 5 wt% nano-sized ZnO to suppress the injection of the space charge within the dielectric matrix. According to Figure 5d, space charge distribution’s region near the 10 wt% doped specimen’s negative

![Figure 3](http://dx.doi.org/10.5772/intechopen.80217)

**Figure 3.** The relative permittivity of EVA/ZnO composites.
electrode is bigger compared with that of the Figure 5c. According the space charge pattern analyzed in group e, it is obvious to see a uniform charge close to either electrode. The homocharges migrate gradually toward the specimen matrix.

Since the electric field under the material’s DC stress for cable accessories concerns a lot for the practical adoption, the distribution of the electric field $E(x)$ which is presented in Figure 6 of EVA composites across the specimen had been worked out on the basis of Poisson’s Eq. (1):

$$E(x) = -\frac{1}{\varepsilon_0 \cdot \varepsilon_r} \int_0^x \rho(x) \, dx$$

Where $\varepsilon_r$ and $\varepsilon_0$ are the relative and vacuum permittivity; $\rho(x)$ is charge density; $x$ is the specimen’s thickness and $d$ is the boundary [19]. The accumulation of the space charge distorted the electric field in undoped EVA more seriously compared with others. The distribution of electric field in 1 wt% filled specimen becomes nicer through the comparison with the undoped one. It seems that the electrical field in 5 wt% filled one is the best result. Additionally, the electrical stress is the highest in hybrid filling.

In general, homocharges usually generate from charges which are injected from metal electrodes. Moreover, they depend on the balance between charge injection and carrier diffusion to the EVA matrix. That is to say, the homocharges remain when people extract negative or positive carriers into the positive electrode/negative electrode electrodes. In terms of the base EVA, the homocharges which are injected from positive electrode move through the polymer matrix.
Figure 5. EVA/ZnO composites’ space charge profiles during the polarization.
matrix. Because there are some similarities between the molecular chains in EVA matrix and the things in PE, which contain electrons that move along the inter chains [20], it’s not difficult for the electrons to extract into the positive electrode, which may form positive homocharges and transport into the polymer matrix. Because there are some chemical groups or free chains in the pure EVA within the experiment, acting as space charge or charge carries may be injected very easily. Nevertheless, it’s easy to observe the homocharges near the negative electrode when considering the less doping content of ZnO. The electrons are captured by the ZnO nanoparticles and prevented from extracting into the positive electrode.

It’s clear that the space charge injection is restrained to a great degree by the sample which contains 5 wt% nanoparticles. Since a lot of traps may be introduced by the ZnO nanoparticles’ incorporation into EVA matrix, it is able to capture enough homopolar charges for the purpose of impairing useful electric fields between the specimen’s surfaces and the electrodes and devote to the carrier injection’s restraint from electrodes. It is possible to form the percolation network with higher fillgrade, which may cause more negative injection close to the negative electrode. Compared with the nanocomposites, the EVA with hybrid doping has done worse. The micro-sized fillers may impair the nanoparticle interface effect and destroy the major polymer chain, which makes the homocharges inject from the electrodes. The space charges’ distribution corresponds well with the dielectric properties’ outcomes.

3.3. Space charge dissipation

EVA nanocomposites’ space charge profiles are displayed in Figure 7b and c as well as d. Both homocharges can be found within the specimen at the initial stage. The beginning stage’s
Figure 7. Space charge behaviors of EVA/ZnO composites during depolarization.
decay speed is more quickly compared with the pure EVA. A minute later, the residual charge will reduce in a rather slow rate. More complicated depolarization procedures can be seen in Figure 7e. In terms of the EVA doped with micro-sized and nano-ZnO particles, there are some similarities between the nanocomposites and the quick dissipation at the beginning stage. Even so, homocharges have been injected to the matrix’s deeper areas instead of being transported into electrodes.

EVA/ZnO composites’ space charge profiles are shown in Figure 7 in the process of the depolarization when removing thirty-minute stressing. It’s obvious that the charges dissipate rather quickly at first for the pure sample in Figure 7a and positive charges occupy most of the polymer matrix. Later on, both the positive and negative carriers migrate through the electrodes and keep a little totally. The entire charge within the matrix will be worked out by Eq. (2) for further discussion.

$$Q = \int_{0}^{d} |p(x)| \cdot S \cdot dx$$  \hspace{1cm} (2)

Where $d$ is the specimen’s thickness, $S$ is the electrode area and $p(x)$ is charge density. The entire charge’s outcome after being stressed at $-25 \text{kV/mm}$ for 30 min is presented within Figure 8. It’s clear that the 5 samples dissipate fast at the beginning and the base EVA’s charge dissipation continues all the time. Nevertheless, the amount of charge remains rather constant nearly a minute later for the doped specimens. It is obvious that the specimens’ entire charges in higher fillgrade sample decay more quickly compared with the samples with lower ZnO contents. The decay of the charges with hybrid doping within specimens presents the trend with pure EVA. However, the 10 wt% specimen causes the residual charges in minimum.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Total space charge decay process of different samples.}
\end{figure}
After we remove the applied stress from the specimen, the space charges transport with time mostly because of the detrapping process. The differences in the decay rate at various times can depend on the time constants for the trapping of deep and shallow traps. The quick dissipation in the initiative stage corresponds with the detrapping from the shallow traps. In addition, capturing charge carriers are hard in deep traps, which results in a slow rate of charge dissipation in doped specimens. More deep traps and shallow are introduced by nano-sized ZnO particles doping into the polymer. However, deeper traps are produced by the micro-sized ZnO particles through the comparison with the nanocomposites, as the form of brand-new disadvantages, causing more remnant charges. In terms of the base EVA, the traps’ energy level is homogeneous to some extent. Therefore, the speed for the base EVA does not have too many changes at the time of dissipation.

A lot of studies have shown that the space charge correlates with the mobility, the conduction as well as the trap features [7]. The model is derived thinking about the trapping-detrapping equilibrium among the trap levels because of the thermal excitation. In accordance with the space charge density’s changes and the Poisson’s equation with the time of the depolarization, the carriers’ obvious mobility as well as the relative trap depth is able to be analyzed as follows:

\[
\mu(t) = \frac{2\varepsilon}{q^2(t)} \frac{d\sigma(t)}{dt}
\]

(3)

\[
n(t) = kT \ln \left( \frac{\mu(t)}{eR^2} \right)
\]

(4)

Where \( R \) is the mean distance between localized states (5 \( \times \) 10^{-7} m), \( \varepsilon \) is the electron’s quantity, \( h \) is the Planck constant, \( T \) is the absolute temperature, \( \varepsilon \) is the permittivity, \( k \) is Boltzmann constant and \( q(t) \) is the average charge density [21]. The obvious mobility’s outcome which is worked out by equation from the data of Figure 8 is analyzed in Figure 9. It is obvious that undoped EVA’s mobility keeps invariant with the time of the depolarization, which is in accordance with EVA copolymer’s uniform structure. Nanocomposites’ migration rate is high at the original period and the mobility becomes lower with further improvement. 10 and 1 wt% ZnO nanoparticles doped specimens have the highest mobility in accordance with the total space charges’ quick dissipation at the initial stage. The specimen’s trend with 5 wt% nanoparticles presents a proper central symmetry on the basis of the neat EVA. In terms of the entire mobility expression of the nanocomposite, this value decreases as the time increases, because the doping of nanoparticles leads to deeper traps in the charge release mechanism. It is predicted that the micro-sized particles act as constraint carriers migrating and big disadvantages in the process of the depolarization. According to Figure 10, it is clear to see the outcomes of the relative trap depth by Eq. (4). Compared with the change in apparent mobility over time, the results of the depth of the trap show the opposite trend. The base EVA’s trap depth on average is nearly 0.81 eV and the deep traps’ depth in the EVA composites can be improved by the filler doping. A wide range of trap depth is produced by the 1 wt% nanoparticles doping because of the localization state’s changes, where deep traps play an important role in the space charge injection’s suppression. A majority of the volume may be covered by the matrix.
Figure 9. Apparent mobility with depolarization time.

Figure 10. The trap depth with depolarization time.
filler interface region at the time of introducing more filler. Moreover, the deep trap depth can be increased on average, which will prevent the injection of space charge from the electrodes. Nevertheless, the percolation network may be formed or the interface is possible to overlap with the fillgrade reaching 10 wt%, which may reduce the negative homocharge injecting barrier as well as the trap depth. As is mentioned before, the chain may be broken by the extra micro-sized particles and brand-new disadvantages may appear which may act as local deep traps and is not sufficient to construct an injection barrier. In addition, the charge injecting can be accelerated by the weaker interface effect.

In order to confirm these assumptions, the conduction current had been evaluated at ~25 kV/mm. It can be seen within Figure 11. It’s clear that the base EVA conductivity can be greater in general compared with the doped specimen’s conductivity. EVA composites’ resistance may be increased by both the nanometer and micron-sized ZnO particles at EVA filler ratios. There is a certain relationship between charge mobility and conduction current. A change in conduction can be caused by the interfacial interaction between the polymer body and the filler, or the space charge which is accumulated close to the electrode may limit the conduction current. A charge blocking area can be formed by the trapped charge through the increase of the barrier to the carrier injection. Additionally, the negative and positive charges are localized because of the low charge mobility, which will impair carrier migration. Nevertheless, it seems that the extra micro-ZnO may decrease the mobility of the charge carrier, which in turn increases in the entire conductivity. EVA composites’ charge carrier mobility may be reduced by the ZnO particles. The outcomes above can strongly prove the space charge suppression mechanism.

Figure 11. DC conduction currents of EVA/ZnO composite under ~25 kV/mm.
4. Conclusions

In the paper, EVA composites which contain 10, 5, 1, and 1 wt% ZnO nanoparticles had been prepared where specimens doped with the comparison of 5 wt% micro-sized and nano-sized ZnO. Micron and nano-ZnO particles on EVA composites' space charge actions and dielectric properties had been researched. Below are the major conclusions.

1. According to the analysis of the SEM, the micro-scaled and nano-particles had been in homodisperse within the EVA composites. The ZnO doping can increase the dielectric constant and the dissipation element of EVA composites with 5 and 1 wt% nanoparticles may be lower at lower frequencies through the formation of the areas which are restricted by polarization and the impediment of the carriers' transport through various kinds of interfaces and chains.

2. When ZnO nanoparticles are introduced, co-directional charge injection takes place at the negative electrode rather than at the positive electrode, thus the change in electron extraction induced by the matrix-filler interface. In 5 wt% nanoparticle-doped EVA, the electric field is uniformly distributed under high electrical stress.

3. During depolarization, the total residual charge of the 10 wt% doped specimen was less than the final remaining charge at last. For dissipating speeds, for micron- and nano-sized particle doping, it is faster at higher filling levels, which has been decided by the obvious mobility and the conductivity.

4. Through correctly doping the nanoparticles, the injection of space charge can be suppressed through the help from the deeper average trap depth. The chain may be damaged by extra micro particles and brand-new disadvantages can be created, which may act as charge carriers.

5. Considering about the outcomes mentioned before, we can conclude that doping with proper ZnO may suppress the injection of space charge, cause to lower loss elements, increase the resistivity of volume and uniform the distribution of electric field. Thus, EVA/ZnO nanocomposites can be hopeful candidates for the applications of HVDC cable attachment insulation. Mechanical properties and breakdown strength should be further studied.

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