Effect of Deep Traps and Molecular Motion on Dc Breakdown of Polyethylene Nanocomposites

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Abstract. Low-density polyethylene (LDPE) has been widely used as an insulating material in high-voltage direct-current power cables. In this research, we investigate how to improve the electrical breakdown strength of LDPE by nanodoping method and the mechanism of improvement. MgO particles with an average diameter of 50 nm are mixed with LDPE to fabricate nanocomposites by using a toque rheometer. Five kinds of nanocomposite samples are fabricated with nanofiller loadings of 0.25 wt%, 0.5 wt%, 1 wt%, 2 wt%, 3 wt% and pure LDPE is made as the contrast. Then the nanocomposites are pressed into sheet samples about 100 µm by plate vulcanizing machine. The images observed by scanning electron microscope show nanoparticles are dispersed uniformly in LDPE matrix. X-ray diffraction is used to measure the bonding effect between nanoparticles and polymer matrix as well as the morphology of nanocomposites. The trap parameters such as trap levels are characterized by thermally stimulated depolarization current. The dc breakdown experiments indicate that the dc breakdown strength increases firstly and then decreases with an increase in nanofiller loading. The dc breakdown strength is enhanced by incorporating nano MgO and reaches the maximum value 377.06 kV/mm at around 0.5 wt%, which is 17.61% higher than the breakdown field of pure LDPE. The influences of bonding effect, morphology, and trap properties on dc electrical breakdown strength of LDPE nanocomposites are analyzed. It is found that incorporating a small amount of MgO nanoparticles into LDPE matrix enhance the bonding effect between nanoparticles and polymer matrix and establish isolated interfacial regions around nanoparticles. Then, deep traps are formed in the interfacial regions and molecular chains with occupied deep charges are difficult to move under electric force. Consequently, the dc electrical breakdown performance is improved. At higher nanofiller loadings, bonding effect is weakened and interfacial regions are overlapped so that carriers can migrate more easily and the dc electrical breakdown field is reduced.

Keywords: Charge transport · DC electrical breakdown · Molecular displacement · Low-density polyethylene · Nanocomposite dielectrics

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1 Introduction

High-voltage direct-current (HVDC) power transmission systems increasingly occupy the power transmission market owing to its advantages of low electrical loss, stability and less expensive [1–3]. Low-density polyethylene is one of the widely used basic electrical insulating material for HVDC power cables [4, 5] as for its' great electrical insulation characteristics [6, 7]. Studying the electrical breakdown strength of this kind of insulating material has a great influence on its' application.

Doping nanofillers is an useful method to improve the dc breakdown strength of LDPE insulating materials [8–10], which enhances the electrical breakdown strength firstly and then declines it with the increasing of nanofiller loadings [11, 12]. In addition, nanofillers doping can also affect the crystalline properties, dc conductivity properties and trap distributions of nanocomposites [13–16]. Xu et al. observed that the crystallinity of the LPDE/MgO nanocomposites initially increases and then decreases with the increasing of the loading. Nilsson et al. found that the dc conductivity reduces firstly and then increases when the nanofiller loading increases. In [15], LDPE/Al_2O_3 nanocomposites was investigated and the author obtained that the deep trap energy level has an increase and then lower down with increase of nanoparticle loading. The simulation to study the relation of molecular displacement with dc breakdown of LDPE and investigations about the effects of the thickness and temperature on dc breakdown [17, 18] have already emerged. However, it is still unclear how deep traps and crystalline structure affect dc breakdown strength. To further explore the problem, in the work, the LDPE/MgO nanocomposites were prepared to investigate the relation of electrical breakdown strength, crystallinity, crystallite size, trap distributions and dc conductivity.

2 Experimental

2.1 Materials

LDPE (FT6230) having melt flow rate of 2.0 g/10 min at 190 °C/2.16 kg and density of 0.922 g/cm^3 was used as the polymeric matrix. Milky-white spherical LDPE has a low crystallinity and a melt temperature about 111 °C. MgO nanoparticles modified by γ-(2,3-expoxypropoxy) propyltrimetho-xysilane having purity of 99.9%, average size of 50 nm and specific surface area of 50 m^2/g were selected as the doping nanofillers.

2.2 Sample Preparation

Two-step melt blending method was carried out to make MgO/LDPE nanocomposites. The main details are as follows. LDPE and MgO nanoparticles were dried in a vacuum oven at 80 °C and 10 °C, respectively. Then nanoparticles were mixed with LDPE matrix in the Torque Rheometer (RM-200C). The processing conditions were set as following: experimental temperatures in 1, 2 and 3 districts: 110 °C, 100 °C and 110 °C, motor speed: 100 rpm and mixing time: 30 min. In order to get a better dispersion effect of nanoparticles, the mixing processes were divided into two steps. First, prepare nanofiller loading of 20 wt% nanocomposites. And then, samples with loadings of 0.25 wt%, 0.5 wt%,1 wt%, 2 wt% and 3 wt% were obtained by using pure LDPE matrix to dilute the loading of 20 wt% prepared in the first step and the neat LDPE was made as the contrast.

Then films about 100 μm in thickness were prepared by Plate Vulcanizing machine (YT-LH-20B). The experiments were performed the following steps. First, block samples were preheating for 25 min without pressure. Then, to avoid bubbles in the sheet samples during the pressing process, a step-by-step boosting method is adopted, successively pressed at 5 Mpa, 10 Mpa and 15 Mpa for 5 min each pressure. Finally, shut down the power and let the sample cooling down naturally. In this way, two sizes of specimens were made, round sheets about 50 mm in diameter and square ones with each length of 8 cm in shape. Based on the reason of eliminating the thermal history, specimens for direct current (dc) breakdown experiments were placed into a vacuum oven at 95 °C for 30 min, and then cooled down to 30 °C in a vacuum environment. Then other films were put into an oven at 60 °C for 24 h.

2.3 Characterization

The scanning electron microscope (SEM) experiment was utilized to examine the dispersion of MgO nanoparticles inside the LDPE matrix. The films were frozen in liquid nitrogen, broken and then sputtered the fractured sections with gold which would be observed under the potential of 5 kV or 15 kV.

X-ray diffraction (XRD, D8 ADVANCE A25) was applied to measure the crystallinity and crystallite size of samples. The measured angle (2θ) ranged from 10° to 50° with the scanning rate of 0.02°/s. After all measurements finished, the DIFFRAC EVA software was used to analyze the data.

The conductivity is calculated out through the volume resistivity experiment. Volume resistivity of dielectric nanocomposites were tested by the Model 65 High Resistivity Measurement. The measurements were performed under ac voltage about 500 V at room temperature. The square sheet samples with a side length of 8 cm were applied in volume resistivity tests. Each sample was measured for 11 times and 3 times of them should be discarded to decrease the error.

The trap parameters were measured with thermally stimulated depolarization (TSDC, Concept 90) in a temperature range from −100 °C to 90 °C. The test conditions are following: polarization voltage: 250 V, polarization temperature: 70 °C, polarization time: 20 min, and short-circuiting time: 3 min. The film samples should be sputtered gold both sides firstly before the test.

The dc electrical breakdown strengths of samples were tested through two spherical copper electrodes at room temperature. The measurement was performed at the dc ramp rate of 500 V/s till the sample failed. Each kind of specimen was tested at least 20 times in this experiment.

3 Results

3.1 Dispersion of Nanofillers in Polyethylene

The dispersion of MgO nanoparticles inside the film samples has been observed by SEM, as shown in Fig. 1. The MgO nanoparticles can be clearly seen in the samples and its number increases with the filler loading increasing. Generally speaking, nanoparticles disperse well in LDPE matrix. Of course, it can be observed that the size of most nanoparticles in samples is less than or just about 100 nm.

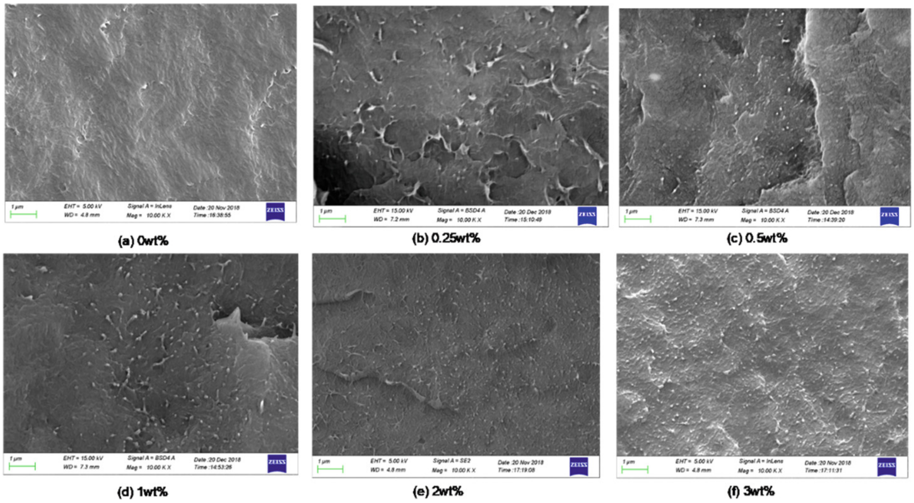
(a) 0wt% (b) 0.25wt% (c) 0.5wt%
(d) 1wt% (e) 2wt% (f) 3wt%

Fig. 1. SEM images of six kinds of MgO/LDPE nanocomposites: (a) 0 wt%, (b) 0.25 wt%, (c) 0.5 wt%, (d) 1 wt%, (e) 2 wt%, (f) 3 wt%.

3.2 Crystalline Properties

XRD measurement was performed in characterizing the crystalline properties of samples, as shown in Fig. 2. It is clearly seen that the crystallinity firstly increases and then begins decreasing at loading of 0.5 wt% with the increase of nanofiller loading, and the crystallinity reaches the maximum value at 0.5 wt% in XRD spectra. The crystallinity nearly keeps unchanged above the loading of 0.5 wt% (40.2%). It can be easily concluded that adding a small amount of nano MgO can increase the crystallinity of the LDPE dielectric nanocomposite. Figure 2(b) shows the crystallite sizes of samples which are calculated by following formula [19].

$$D = \frac{0.89\lambda}{\omega\cos\theta} \tag{1}$$

where D is the crystallite size, λ represents the wavelength of X-rays (λ = 0.15406 nm), ω denotes the full width at half maximum (FWHM), and θ indicates the Bragg angle.

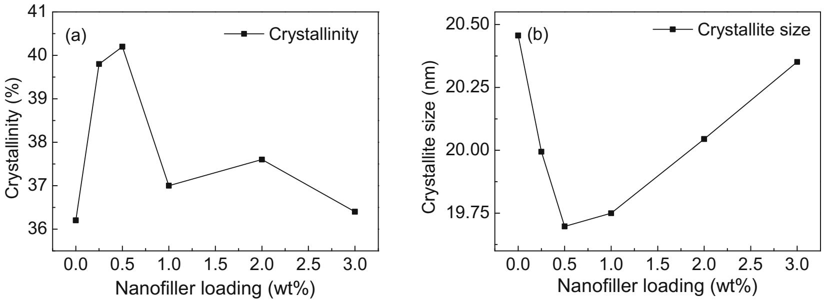

Fig. 2. Results measured by XRD. (a) Calculated crystallinity of different nanofiller loadings of LDPE/MgO from XRD. (b) Calculated crystallite size.

From the crystallite size curve, it is easily can be find that the crystallite size of samples decreases firstly and then increases with the nanofiller loading increasing and has the minimum value at 0.5 wt%. The change trend of crystallite size is just against with that of crystallinity.

3.3 DC Conductivity

Figure 3 shows the dc conductivity of film samples with different nanofiller loadings. It can be easily observed that the conductivity firstly decreases until at 0.5 wt% and then increases with the increasing of nanofiller loading. And the dc conductivity of samples reaches the minimum value about $5.49 \times 10^{-15} \mathrm{Sm}^{-1}$.

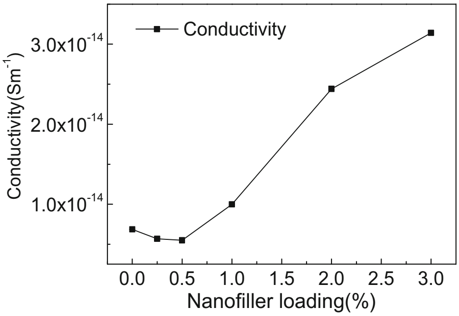

Fig. 3. Conductivity as a function of nanofiller loading.

3.4 TSDC Measurement

Figure 4 shows the TSDC results. It is easy to look out two obvious relaxation peaks (known as α and γ) from the TSC curves, and the temperatures of the α peaks are shown in Table 1. The location of another relaxation peak is between the α and γ

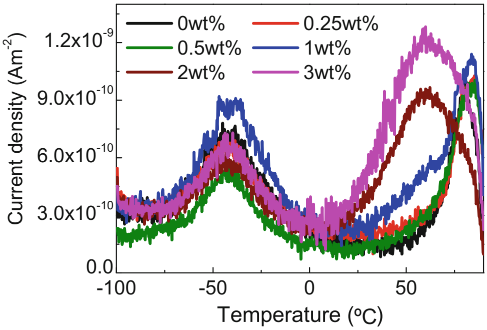

Fig. 4. Results of TSDC measurement.

peaks, named as the β peak. The incorporation of nano-magnesia has an impact on TSC curves. The α peak reveals the deep traps distribution. The trap parameters can be obtained by fitting TSC results to the following equation [20]:

$$j(T) = B\exp\left[-\frac{E_b}{k_BT} - \frac{1}{\alpha\tau_0}\int_{T_0}^{T_1}\exp\left(-\frac{E_b}{k_BT}\right)\mathrm{d}T\right] \tag{2}$$

where *j(T)* is the TSDC current density in Am^{-2}, B is a constant in Am^2, E_b is the activation energy of relaxation process in eV, α is the heating rate in Ks^{-1}, τ_0 is the relaxation time constant in s, k_B is the Boltzmann constant, T_1 is the temperature of sample after heating in K, T_0 is the initial temperature of sample at the beginning of heating in K, and T is the temperature in K.

The parameters of trap energy of samples are shown in Table 1. The trap energy levels decrease with an increasing in nanofiller loading.

3.5 DC Breakdown

In this work, two parameter Weibull distribution is applied to analyze the dc breakdown strength and is described as follows [21]:

$$P_E = 1 - \exp\left[-\left(\frac{E}{E_c}\right)^{\varphi}\right] \tag{3}$$

$$P_E(i,n) = \frac{i-0.44}{n+0.25} \tag{4}$$

where E is the dc breakdown field value arranged from small to large in kVmm^{-1}, P_E indicates the accumulative probability of dc breakdown strength at E, E_c represents the characteristic electrical breakdown strength with accumulative probability of 63.2%, φ is shape distribution parameter, and n is the testing time for the same sample.

Table 1. The temperatures of α peaks and its calculated trap energy levels

Samples(wt%)	Temperature(°C)	E_{trp}(eV)
0	81	1.24
0.25	84	1.33
0.5	83	1.4
1	83.5	1.13
2	63	0.53
3	64	0.45

The Weibull cumulative probability of dc breakdown strength of the LDPE/MgO nanocomposites is shown in Fig. 5. In addition, the fitting curves choose the transformation of log[−ln(1 − P)] as the ordinate and the breakdown strength as the abscissa. And Fig. 6 shows the dc characteristic breakdown field of LDPE/MgO dielectric nanocomposites.

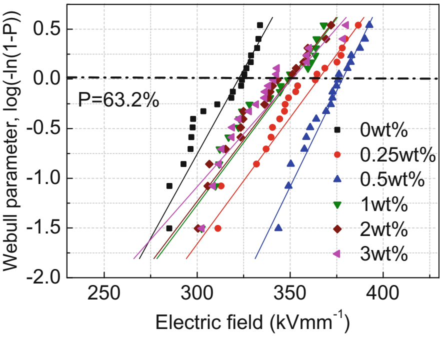

Fig. 5. Weibull cumulative probability of dc breakdown strength of the LDPE/MgO nanocomposites with various nanofiller loadings.

The dc breakdown strength increases firstly and then decreases with an increase in nanofiller loading. Slight nano-magnesia doping enhances the dc breakdown strength of LDPE/MgO nanocomposites apparently, which reaches the maximum value 377.06 kVmm^{-1} (17.61% higher than the breakdown field of pure LDPE which is 320.59 kVmm^{-1}) at around 0.5 wt%.

4 Discussion

Figure 7 shows the relationship between characteristic breakdown strength, crystallinity and crystallite size. It is easy to know that both dc breakdown strength and crystallinity increase at low nanofiller loading and then decrease when the loading exceeds 0.5 wt% from Fig. 7(a). They get the maximum value at the particle loading of 0.5 wt%. Figure 7(b) indicates that the dc breakdown strength declines with the

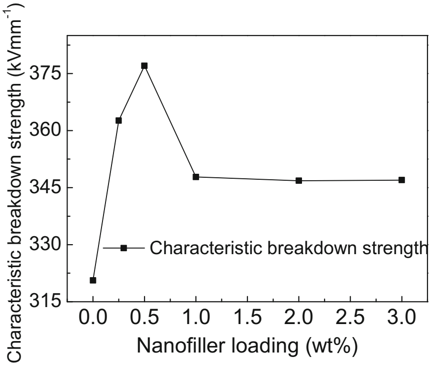

Fig. 6. DC characteristic breakdown strengths in LDPE/MgO nanocomposites.

crystallite size increasing. The correlation between dc conductivity and dc breakdown with trap energy level is shown in Fig. 8. As the increasing of trap energy levels, dc conductivity decreases and dc breakdown strength increases just opposite to dc conductivity.

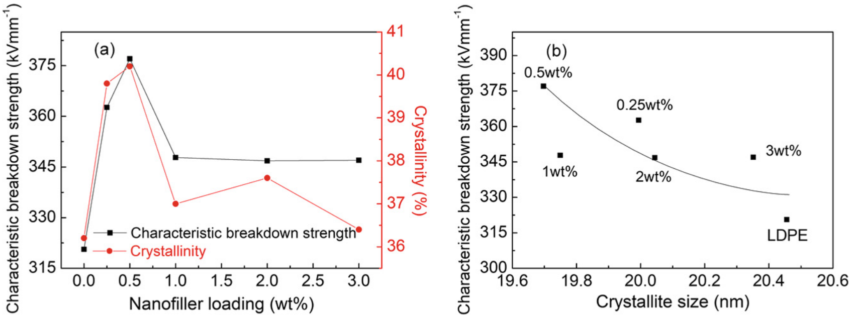

Fig. 7. Relationship between characteristic breakdown strength, crystallinity and crystallite size, (a) characteristic breakdown strength and crystallinity; (b) characteristic breakdown strength and crystalline size.

The crystalline properties and traps are related to the molecular structure of the LDPE/MgO nanocomposite. And the influences reflect on the conductivity and the breakdown strength. The hypothesis can be proposed that adding a small amount of MgO nanoparticles into LDPE matrix can enhance the bonding effect between nanoparticles and polymer matrix and establish isolated interfacial regions around nanoparticles. Then, deep traps are formed in the interfacial regions and molecular chains with occupied deep charges are difficult to move under electric force. Consequently, the dc electrical breakdown performance is improved. At higher nanofiller loadings, bonding effect is weakened and interfacial regions are overlapped so that carriers can migrate more easily and the dc electrical breakdown field is reduced.

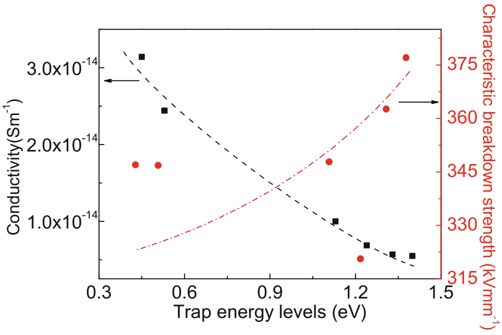

Fig. 8. DC conductivity and dc breakdown strength as a function of trap energy levels.

5 Conclusion

In this work, the LDPE/MgO nanocomposites of nanofiller loadings of 0 wt%, 0.25 wt%, 0.5 wt%, 1 wt%, 2 wt% and 3 wt% were prepared. Then SEM, XRD, TSC, dc breakdown, and dc conductivity experiments were processed to test the properties. And it can be concluded as follows:

1. With the increasing of nano MgO loadings increasing, the crystallinity increases and crystallite size decreases initially and then begins to decrease and increase at the loading of 0.5 wt%, respectively. Nanofillers has an impact on the morphology which is reflected in deep traps, and further embodied in the dc conductivity and dc breakdown strength.
2. A slight incorporation of nano MgO can enhance the dc breakdown strength about 17.61% compared with pure LDPE matrix which happens at the loading of 0.5 wt%. As the increasing of trap energy levels, dc conductivity decreases and dc breakdown strength increases.

In conclusion, the deep traps and molecular motion have effects on the dc breakdown properties of LDPE/MgO nanocomposites.

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