

Article

A Comparison of Electrical Breakdown Models for Polyethylene Nanocomposites

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Abstract: The development of direct current high-voltage power cables requires insulating materials having excellent electrically insulation properties. Experiments show that appropriate nanodoping can improve the breakdown strength of polyethylene (PE) nanocomposites. Research indicates that traps, free volumes, and molecular displacement are key factors affecting the breakdown strength. This study comprehensively considered the space charge transport, electron energy gain, and molecular chain long-distance movement during the electrical breakdown process. In addition, we established three simulation models focusing on the electric field distortion due to space charges captured by traps, the energy gain of mobile electrons in free volumes, the free volume expansion caused by long-distance movement of molecular chains under the Coulomb force, and the energy gained by the electrons moving in the enlarged free volumes. The three simulation models considered the electrical breakdown modulated by space charges, with a maximum electric field criterion and a maximum electron energy criterion, and the electrical breakdown modulated by the molecular displacement (EBMD), with a maximum electron energy criterion. These three models were utilized to simulate the breakdown strength dependent on the nanofiller content of PE nanocomposites. The simulation results of the EBMD model coincided best with the experimental results. It was revealed that the breakdown electric field of PE nanodielectrics is improved synergistically by both the strong trapping effect of traps and the strong binding effect of molecular chains in the interfacial regions.

Keywords: polymer nanocomposites; traps; DC breakdown; energy gain; molecular motion; free volume



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1. Introduction

Power cables are the main equipment in urban transmission grids and offshore wind power transmission [1–6]. Direct current (DC) power cables have the advantages of long transmission distance, large transmission capacity, and low power loss, and they are the key electrical equipment for large-scale reception of new energy power generation. Under the action of DC voltage, the power cable has no capacitive current and can realize long-distance power transmission. The aging of the insulating material of power cables under the DC electric field is slow, and its lifespan is greatly prolonged [1,3–6]. Moreover, the breakdown electric field of the insulating material under DC voltage is 2–3 times higher than that under AC voltage [7], which improves the safety margin of the DC power cable. Low-density polyethylene (LDPE) is the main insulating material of power cables, and its electrical insulation performance is important for the safe and reliable operation of power cables [1–6]. Polymer nanocomposites (PNCs) have excellent properties, such as lower electrical conductivity, higher breakdown electric field, less space charges, higher thermal

stability, and higher mechanical strength [5,6,8–12]. PNCs, known as third-generation insulating materials, have broad application prospects. The experimental results demonstrate that doping a relatively low content of nanoscale fillers in polyethylene can form deep traps, leading to the reduction in the electrical conductivity of the nanocomposites and the improvement in the breakdown strength [5,6,9,11–14]. Advanced LDPE nanocomposites can be used as insulating materials for DC power cables [5,6,12] and energy storage capacitors [15,16], improving the capacity of power cables to transmit electrical energy and the energy storage density of capacitors. Power cables and energy storage capacitors are key equipment for the centralized transmission of large-scale offshore wind power, providing support for the supply of clean energy to cities.

It is generally believed that the excellent electrical properties of polymer nanocomposites originate from the interfacial region between the nanoparticles and the polymer matrix [6,12]. The multi-core interfacial region model proposed by Tanaka et al. [17,18] and the multi-region structure model proposed by Li et al. [19] show that deep traps are formed in nanocomposites when a small amount of doping is used. Deep traps near the electrodes trap more charges and reduce the number of charges injected. This can suppress the space charge accumulation, reduce the electric field concentration, and improve the breakdown electric field. By comparison, traps with higher energies can reduce the effective charge carrier mobility, reduce electrical conductivity and Joule heating, and improve breakdown performance. The interfacial region models proposed by Nelson et al. [20] and Min et al. [21] show that the interfacial regions not only form deep traps, but also constrain the motion of molecular chains. Under the action of the Coulomb force, the molecular chains undergo directional displacement, which affects the size of the surrounding free volumes. This, in turn, changes the breakdown performance of nanodielectrics. The interfacial region models show that increasing the trap level and/or the interaction between molecular chains in the interfacial regions can improve the breakdown strength of polymer nanocomposites.

Experiments and simulations indicate that the breakdown of polymer materials under a strong electric field is related to physical processes such as electric field distortion and electron energy gain. Tanaka et al. [22] used pulsed electroacoustic equipment to test the space charge distributions and the electric field distributions of LDPE under the action of a strong electric field. It was found that positive space charge packets are formed in LDPE when the electric field is higher than a threshold value. As the positive space charge packets move toward the cathode, the electric field in front of the charge packets gradually increases, and the material is broken down when the maximum distorted electric field in LDPE reaches the breakdown electric field. Chen et al. [23] considered the formation and migration of space charges in LDPE, and established a polymer breakdown model based on the accumulation of space charges and the corresponding electric field distortion. The relationship between the DC breakdown electric field of LDPE and the thickness of samples was calculated. It was found that the breakdown electric field has an inverse power function relationship with the thickness. Choi et al. [24] also used a breakdown model based on the electric field distorted by the space charges to calculate the breakdown characteristics of multilayer polymers with partial barrier contact, and found that partial barrier contact between multilayer structures enhanced the breakdown strength of multilayer dielectrics. From the viewpoint that the electric field force acts on the trapped charges and affects the molecular chain motion, and to comprehensively consider the charge transport, the long-range motion of molecular chains, and the electron energy accumulation, we established a charge trapping and molecular displacement breakdown (CTMD) model for polymer nanocomposites [13,25]. The energy accumulation process of electrons in the free volume expanded by the long-range motion of the molecular chain was simulated, and the relation between the breakdown electric field of the polyethylene nanocomposites with the nanofiller content, the applied pressure, the thickness of the sample, and the ramping rate was obtained. The results are consistent with the results of the electric breakdown experiments.

The above analysis shows that the strong trapping effect of traps and the strong interaction between molecular chains in the interface regions are the two key factors to improve the breakdown strength. However, which of the trap trapping effect and the molecular chain interaction is more influential is still unclear. To clarify the factors of the breakdown characteristics of polyethylene nanocomposites having the greatest influence, this study compared three breakdown models, namely, the electric field distortion, the electron energy gain in a fixed-scale free volume, and the energy gain of electrons in an expanded free volume caused by the motion of molecular chains. By comparing the simulation results with the experiments, the electric breakdown mechanism of polyethylene nanocomposites was clarified. In the present work, we determined the quantitative roles of trapping effects and molecular chain interactions on breakdown strength. This paper provides simulation methods and data support for the improvement in the breakdown strength of polymer nanocomposites.

2. Electrical Breakdown Models

Generally, a ramp voltage with a constant rising rate is applied to the electrodes on both sides of the polymer nanocomposite to investigate the electrical breakdown properties. Firstly, when the voltage is gradually increased, the electrons and holes in the cathode and anode, respectively, are injected into the nanocomposite. After these electrons and holes enter the nanocomposite, they drift under the driving of the electric field. Since there are deep traps formed by many polar groups inside the nanocomposite, the deep traps capture electrons and holes, thereby accumulating space charges of the same polarity inside the nanocomposite [26]. The space charges cause the electric field inside the nanocomposite to be distorted. When the distorted electric field reaches a certain level, it may lead to the breakdown of the nanocomposite. Nanodoping changes the trap properties inside the nanocomposite, which in turn changes the charge injection, the space charge accumulation, and the electric field concentration properties; these changes ultimately lead to the variation in the breakdown strength with the nanofiller content. This breakdown model is called the electrical breakdown modulated by space charges with a maximum electric field criterion (EBEF).

Secondly, there are spaces inside the polymer nanocomposite that are not occupied by atoms, known as free volumes. When charges are transported inside the nanocomposite, they may enter the free volumes. Charges in the free volumes can be rapidly accelerated by electric fields to obtain high energies. If the energy gained by the charges in the free volumes exceeds the trapping ability of the deep traps, the high-energy charges will result in the breaking of the molecular chain and cause the electric breakdown of the nanocomposite [27]. Nanodoping changes the trap energy, which in turn affects the ability of traps to trap the high-energy charges, and ultimately changes the breakdown strength of the nanocomposite. In this process, the effects of space charge accumulation and electric field concentration on the breakdown strength also need to be considered. This breakdown model is called the electrical breakdown modulated by space charges with a maximum electron energy criterion (EBEG).

Thirdly, since the substance entities trapped inside the polymer nanocomposites are polar groups, when the traps capture charges, the Coulomb force on the trapped charges must be transferred to the molecular chains. The molecular chains will undergo directional displacement under the effect of the Coulomb force, resulting in the expansion of the free volumes. An increase in the size of free volumes allows the charges entering them to accumulate more energies. When the energies accumulated by the charges exceed the trapping ability of the deep traps, it causes the breakdown of the polymer nanocomposite. Nanodoping affects both the molecular chain motion and trap properties in nanocomposites, which in turn affects the energy gain properties of charges and the ability of traps to capture high-energy charges. Finally, the electric breakdown strength of the nanodielectric is changed. This breakdown model is called the EBMD model [13,25].

The three breakdown models of EBEF, EBEG, and EBMD all include charge carrier injection and charge carrier transport processes. The mathematical equations of charge carrier injection and charge carrier transport processes are introduced first. Then, the breakdown criteria of EBEF and EBEG models are given. Finally, the equation of molecular chain displacement under the action of electric force in EBMD model is introduced, and the breakdown criterion is given.

2.1. Charge Injection and Charge Transport in Nanocomposites

Figure 1 presents a schematic diagram of the charge transport inside a polymer nanocomposite [25]. The one-dimensional coordinate x is set in the thickness direction of the nanocomposite, and the thickness of the material is L . The left side of the nanocomposite is the cathode and the right side is the anode. Under the action of an applied voltage, the cathode injects electrons into the nanocomposite, and the anode injects holes. Potential barriers exist between the cathode and anode and the nanocomposite interface, which are $u_{in(e)}$ and $u_{in(h)}$, respectively. The interfacial barrier hinders the transfer of charges from the electrode into the nanocomposite. Under an externally applied strong electric field, a potential barrier lowering u_{Sch} appears in the interface barrier, which promotes the transfer of charges to the bulk of the nanocomposite. When the applied electric field is E , the Schottky barrier reduction u_{Sch} is proportional to the square root of the electric field, $u_{Sch} = (eE/4\pi\epsilon_0\epsilon_r)^{1/2}$. Here, e is the electron charge, ϵ_0 is the permittivity of the vacuum in F/m, and ϵ_r is the dielectric constant of the nanocomposite. We adopt the Schottky thermal emission model to describe the charge injections, $j_{in(e)}$ and $j_{in(h)}$, per unit time and unit area of the cathode and anode, into the nanodielectrics [28].

$$j_{in(e)}(0, t) = AT^2 \exp(-u_{in(e)}/k_B T) \exp(u_{Sch}(0, t)/k_B T) \quad (1)$$

$$j_{in(h)}(L, t) = AT^2 \exp(-u_{in(h)}/k_B T) \exp(u_{Sch}(L, t)/k_B T) \quad (2)$$

where A is the Richardson constant, T is the temperature of materials, and t is the elapsed time of applied voltage.

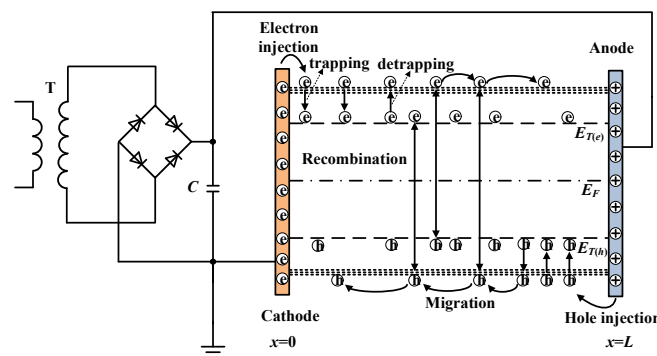


Figure 1. Schematic of the bipolar charge carrier injection and charge carrier transport in polymer nanocomposites under a ramp voltage.

Under an electric field E , there will be a certain concentration of mobile electrons and mobile holes in extended states after the charges in the electrodes are injected into the nanocomposite. Their concentrations are $n_{M(e)}$ and $n_{M(h)}$, respectively. These mobile electrons and mobile holes migrate in the extended states driven by the applied electric field. The mobilities of electrons and holes in the extended states are $\mu_{0(e)}$ and $\mu_{0(h)}$, respectively. Due to the existence of polar groups in polymer nanodielectrics, a certain concentration of deep traps is formed. It is assumed that the energy levels of deep traps of electrons and holes are $u_{T(e)}$ and $u_{T(h)}$, respectively, and their concentrations are $N_{T(e)}$ and $N_{T(h)}$, respectively. Due to the strong trapping ability of deep traps, mobile electrons and mobile

holes may be captured by them during the migration process. The trapping probabilities of electrons and holes in extended states in the electron deep traps and hole deep traps are $P_{T(e)}$ and $P_{T(h)}$, respectively. After a period of time, the deep trapped electron and deep trapped hole densities are $n_{T(e)}$ and $n_{T(h)}$, respectively. In addition, the charges in the deep traps gradually gain energy from the heat bath due to thermal excitation. When the trapped charges gain sufficient energy, trapped electrons and trapped holes can transition to extended states with probabilities of $P_{D(e)}$ and $P_{D(h)}$, respectively. The detrapping probabilities $P_{D(e)}$ and $P_{D(h)}$ decrease exponentially with the increase in the deep trap levels $u_{T(e)}$ and $u_{T(h)}$. When positive and negative charges meet inside the sample, the recombination between these charges occurs. Mobile electrons may recombine with mobile and trapped holes, and mobile holes may recombine with mobile and trapped electrons. The trapped electrons mainly recombine with the mobile holes, and the trapped holes mainly recombine with the mobile electrons.

The time-dependent change in the charge densities of mobile electrons and mobile holes per unit volume is related to the current density flowing into and out of the control volume. Additionally, trap capturing and recombination lead to a decrease in mobile electrons and mobile holes, while the detrapping of trapped charges results in an increase in mobile electrons and mobile holes. The time-dependent changes in trapped electrons and trapped holes per unit volume are related to charge trapping, charge detrapping, and recombination. Charge detrapping and recombination lead to a decrease in deep trapped electrons and deep trapped holes, while charge trapping leads to an increase in deep trapped electrons and deep trapped holes. Four partial differential equations are needed to describe the dynamic processes of mobile electrons, deep trap electrons, mobile holes, and deep trap holes in nanocomposites, respectively [25,29,30]:

$$\frac{\partial n_{M(e)}}{\partial t} + \frac{\partial (n_{M(e)} \mu_{0(e)} E)}{\partial x} = -P_{T(e)} n_{M(e)} \left(1 - \frac{n_{T(e)}}{N_{T(e)}} \right) + P_{D(e)} n_{T(e)} - R_{Me,Mh} n_{M(e)} n_{M(h)} - R_{Me,Th} n_{M(e)} n_{T(h)} \quad (3)$$

$$\frac{\partial n_{T(e)}}{\partial t} = P_{T(e)} n_{M(e)} \left(1 - \frac{n_{T(e)}}{N_{T(e)}} \right) - P_{D(e)} n_{T(e)} - R_{Te,Mh} n_{T(e)} n_{M(h)} \quad (4)$$

$$\frac{\partial n_{M(h)}}{\partial t} + \frac{\partial (n_{M(h)} \mu_{0(h)} E)}{\partial x} = -P_{T(h)} n_{M(h)} \left(1 - \frac{n_{T(h)}}{N_{T(h)}} \right) + P_{D(h)} n_{T(h)} - R_{Me,Mh} n_{M(e)} n_{M(h)} - R_{Te,Mh} n_{T(e)} n_{M(h)} \quad (5)$$

$$\frac{\partial n_{T(h)}}{\partial t} = P_{T(h)} n_{M(h)} \left(1 - \frac{n_{T(h)}}{N_{T(h)}} \right) - P_{D(h)} n_{T(h)} - R_{Me,Th} n_{M(e)} n_{T(h)} \quad (6)$$

The detrapping probabilities $P_{D(e)}$ and $P_{D(h)}$ of the deep trapped charges in the nanocomposite are related to the trap energy levels $u_{T(e)}$ and $u_{T(h)}$ as $P_{D(e,h)} = \nu_0 \exp(-u_{T(e,h)}/k_B T)$. Here, ν_0 is the attempt-to-escape frequency. $R_{Me,Mh}$ is the recombination coefficient between mobile electrons and mobile holes. According to the Langevin recombination model, the recombination coefficient $R_{Me,Mh}$ is determined by $e(\mu_{0(e)} + \mu_{0(h)})/\epsilon_0 \epsilon_r$ [31]. $R_{Me,Th}$ and $R_{Te,Mh}$ are the recombination coefficient between mobile electrons and trapped holes, and that between trapped electrons and mobile holes, respectively. According to the Shockley–Read–Hall model, the recombination rates $R_{Me,Th}$ and $R_{Te,Mh}$ are determined by $e\mu_{0(e)}/\epsilon_0 \epsilon_r$ and $e\mu_{0(h)}/\epsilon_0 \epsilon_r$, respectively [32].

When space charges accumulate inside the nanocomposite, the space charges can distort the electric potential and the electric field. The potential φ inside the nanocomposite can be calculated by Poisson's equation:

$$\partial^2 \varphi / \partial x^2 = -e (n_{M(h)} + n_{T(h)} - n_{M(e)} - n_{T(e)}) / \epsilon_0 \epsilon_r \quad (7)$$

Then, the electric field distribution inside the nanocomposite can be calculated through the negative gradient of the electric potential, namely $E = -\nabla \varphi$.

2.2. Electrical Breakdown Criteria

In the EBEF breakdown model, the electric field concentration effect caused by the accumulation of space charges is mainly considered. It is assumed that when the highest electric field E_{max} inside the nanocomposite reaches a certain threshold value E_C , the material is broken down. The breakdown criterion is $E_{max} \geq E_C$ [23].

In the EBEG breakdown model, the process of electron energy gain under the applied electric field after the mobile charge enters the free volume is mainly considered. When the energy gained by the mobile charges is greater than the trapping ability of the deep traps, the nanocomposite is broken down. Assuming that the free volume length is λ_0 , the energy gained by the electron in the free volume is $e\lambda_0 E(x)$. The maximum energy of electrons inside the nanocomposite is $e\lambda_0 E_{max}$. As shown in Figure 2a, the breakdown criterion of the EBEG model can be obtained as $e\lambda_0 E_{max} \geq u_T$ [27].

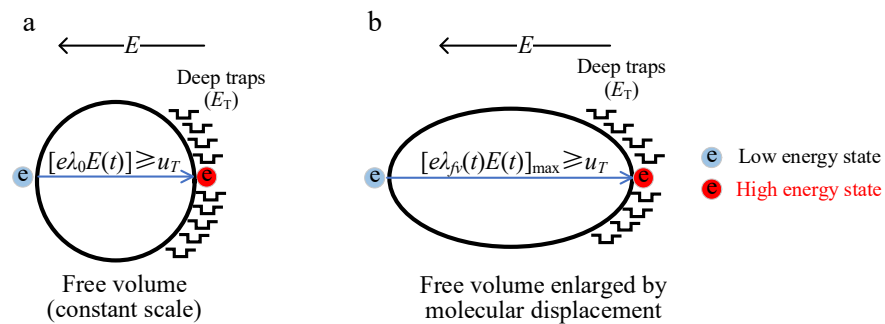


Figure 2. Electrical breakdown criteria of EBEG (a) and EBMD (b) models under a ramp voltage.

In the EBMD breakdown model, the charge carrier injection and transport processes inside the nanocomposite under a strong electric field are considered. Furthermore, after the charges are captured by the deep traps on the molecular chain, the electric force acts on the molecular chain to cause its directional displacement. The time-dependent relationship of the displacement λ_{mol} of the molecular chain is calculated by the following equation [33]:

$$\frac{d\lambda_{mol}}{dt} = \mu_{mol}E - \frac{\lambda_{mol}}{\tau_{mol}} \quad (8)$$

where μ_{mol} is the molecular chain mobility and τ_{mol} is the relaxation time constant of the molecular chain. In addition, μ_{mol} decreases with the increase in the deep trap energy, $\mu_{mol} = \mu_0 \exp(-u_T/k_B T)$, and τ_{mol} increases with the increase in the deep trap level, $\tau_{mol} = \tau_0^{-1} \exp(u_T/k_B T)$.

The directional movement of the molecular chain will cause the expansion of the free volume. It is assumed that the free volume length is equal to the molecular chain displacement, that is, $\lambda_{fv}(t) = \lambda_{mol}(t)$. The mobile charges gain energy in the expanded free volume. If the energy gained by the electrons exceeds the trapping ability of the deep trap, the nanocomposite will be broken down. As shown in Figure 2b, the breakdown criterion of the EBMD model is expressed as $[e\lambda_{fv}(t)E(t)]_{max} \geq u_T$ [25].

3. Results

Both the trap energies and the breakdown strengths of LDPE nanodielectrics doped with various fillers first increased and then decreased with the increase in doping content [5,6,11,12]. It is generally believed that the interfacial region is responsible for the excellent electrical properties of polymer nanocomposites. The trap levels in the interfacial region and the interaction between molecular chains are two key factors to improving the breakdown strength of polymer nanocomposites. However, which factor is more influential remains unclear. The main influencing factors of the breakdown strength are determined by comparing the above-mentioned breakdown simulation models with the experimental results. The quantitative relationship between the influencing factors and

the breakdown strength was obtained. We took the LDPE/Al₂O₃ nanocomposite as an example to compare the three breakdown models. In order to easily compare the simulation results with the experimental results, the parameters in the simulation model were derived from the experimental results [13]. The thickness of the LDPE/Al₂O₃ nanocomposite was 200 μm and the temperature of the sample was 300 K. We investigated the breakdown properties of pure LDPE and LDPE/Al₂O₃ nanodielectrics with nanofiller contents of 0.1, 0.5, 2, and 5 wt%. Since the numerical simulation of the charge drift equation should obey the Courant–Friedrich–Levy (CFL) law, the films were discretized into 300 elements and the computational time interval Δt was set as 1 ms [34]. Figure 3 shows the trap density, trap energy level, and attempt-to-escape frequency of pure LDPE and LDPE/Al₂O₃ nanodielectrics as a function of nanofiller content [13]. N_T , u_T , and ν_0 were obtained from the experimental results of thermally stimulated depolarization currents, and they all first increased and then decreased with the increase in nanofiller content. Charges in the electrodes may first be transferred to the surface traps in the nanocomposite and then injected into the bulk of the material. In this case, the charge injection barriers can be set to the deep trap levels. The mobilities of mobile electrons and mobile holes in the extended states of the nanocomposite were both set to be $1 \times 10^{-13} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$. The trapping probabilities of the deep traps were calculated from the trap densities and the carrier mobilities of the mobile charges. The detrapping probabilities of trapped charges were calculated from the trap levels and the attempt-to-escape frequencies. The recombination coefficients of positive and negative charges were calculated from the mobilities of mobile electrons and mobile holes.

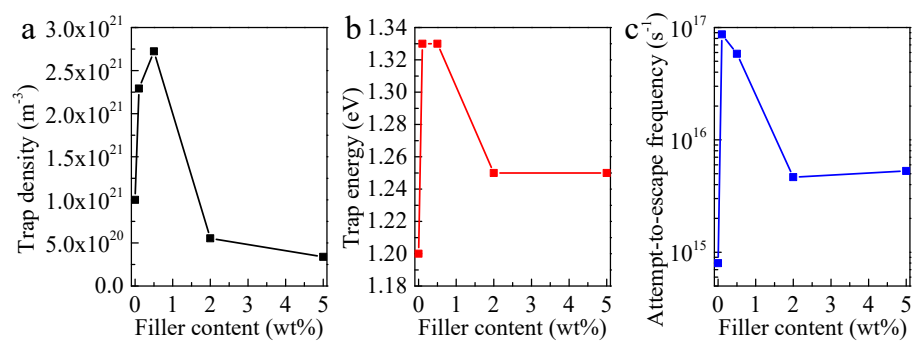


Figure 3. Trap density (a), trap energy (b), and attempt-to-escape frequency (c) versus filler content of LDPE/Al₂O₃ nanocomposites.

It can be seen that the trap energy and density are positively correlated with the breakdown strength of the polymer nanocomposites. However, quantitative studies are still lacking about how much the trap energy and density can change the breakdown strength by affecting the space charge accumulation and electric field concentration. In addition, quantitative studies are also lacking about the extent to which the trap energy and density change the breakdown strength by affecting the electric field distortion and the energy accumulation of electrons in a fixed free volume. Moreover, whether the increase in breakdown strength is caused by the binding effect of nanofillers on molecular chains should also be considered. In order to obtain these quantitative relationships, it is necessary to carry out simulation studies of different breakdown models and compare them with the experimental results to determine the primary and secondary influencing factors. Finally, the quantitative relationship between each influencing factor and the variation range in the breakdown strength can be obtained.

3.1. Simulation Results of EBEF Model

A voltage having a ramping rate of k_{ramp} was applied to the electrodes on both sides of the nanocomposite. As the time t increases, the voltage V_{appl} applied to the electrodes on both sides of the nanocomposite increases gradually, that is, $V_{\text{appl}} = k_{\text{ramp}}t$. The elec-

tric field inside the nanocomposite increases gradually, and the charges injected into the material from the electrodes gradually increase. Due to the slow charge transport inside the nanocomposite, the space charges of the same polarity gradually accumulate inside the material. Homogeneous space charges can distort the electric potential and electric field in the nanocomposite. Figure 4 demonstrates the time-dependent changes in space charge distribution and electric field distribution in the pure LDPE and LDPE/ Al_2O_3 nanocomposites. As the voltage increases gradually, the accumulated space charges in all samples increase greatly, and the distortions of the electric fields become stronger and stronger. When the maximum electric field in the material reaches a certain threshold, that is, $E_{max} \geq E_C$, the sample will be broken down. By comparing the experimental results, E_C was set to 290 kV/mm.

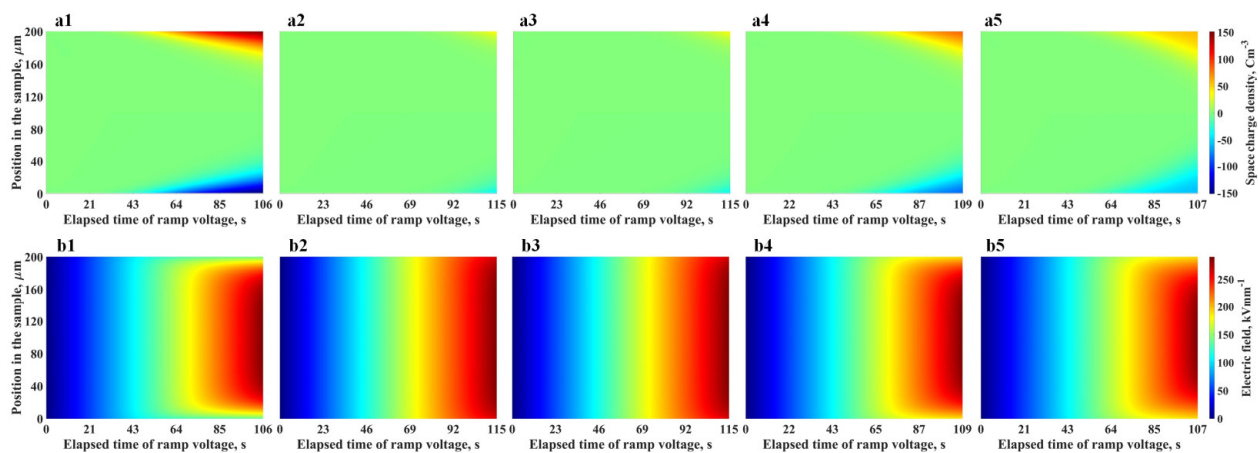


Figure 4. Distributions of space charges (a1–a5) and electric fields (b1–b5) in pure LDPE and LDPE/ Al_2O_3 nanodielectrics with nanofiller contents of 0.1 wt%, 0.5 wt%, 2.0 wt%, and 5.0 wt%.

With a small amount of doping, the trap density and energy levels of LDPE/ Al_2O_3 nanocomposites increase. The ability of the traps to capture charges is enhanced, and more mobile charges are captured by the traps in the insulating material near the electrodes. The trapped charges of the same polarity near the electrodes increase, so that the electric field near the electrodes is greatly reduced. It can be seen from the Schottky emission equation that the charge carriers injected by the electrodes into the nanocomposite are greatly reduced at low electric fields. This can decrease the degree of electric field distortion inside the nanocomposite. Under the same voltage, the maximum electric field E_{max} in the nanocomposite becomes smaller. This increases the breakdown electric field of the nanocomposite. When a large amount of doping is used, the trap density and energy level of the LDPE/ Al_2O_3 nanocomposite gradually decrease, the space charge distribution becomes longer, and the electric field concentration becomes larger, leading to a larger maximum electric field E_{max} in the nanocomposite. This can lead to a reduction in the breakdown strength of nanocomposites having larger filler contents.

3.2. Simulation Results of EBEG Model

It is assumed that a certain scale of free volume exists in the LDPE nanocomposites. Charges in the extended states enter the free volumes and are accelerated by the electric field to gain energy. Figure 5 depicts the time-dependent changes in space charge distributions, electric field distributions, and electron energy distributions in pure LDPE and LDPE/ Al_2O_3 nanocomposites. As time passes, the voltage applied to the electrodes on both sides of the materials increases gradually. The space charge accumulation inside the materials increases, the electric field distortion becomes more serious, and the energy gained by the electrons in the free volume also increases. When the charges gain energy beyond the trapping ability of the deep traps, breakdown of the material will occur.

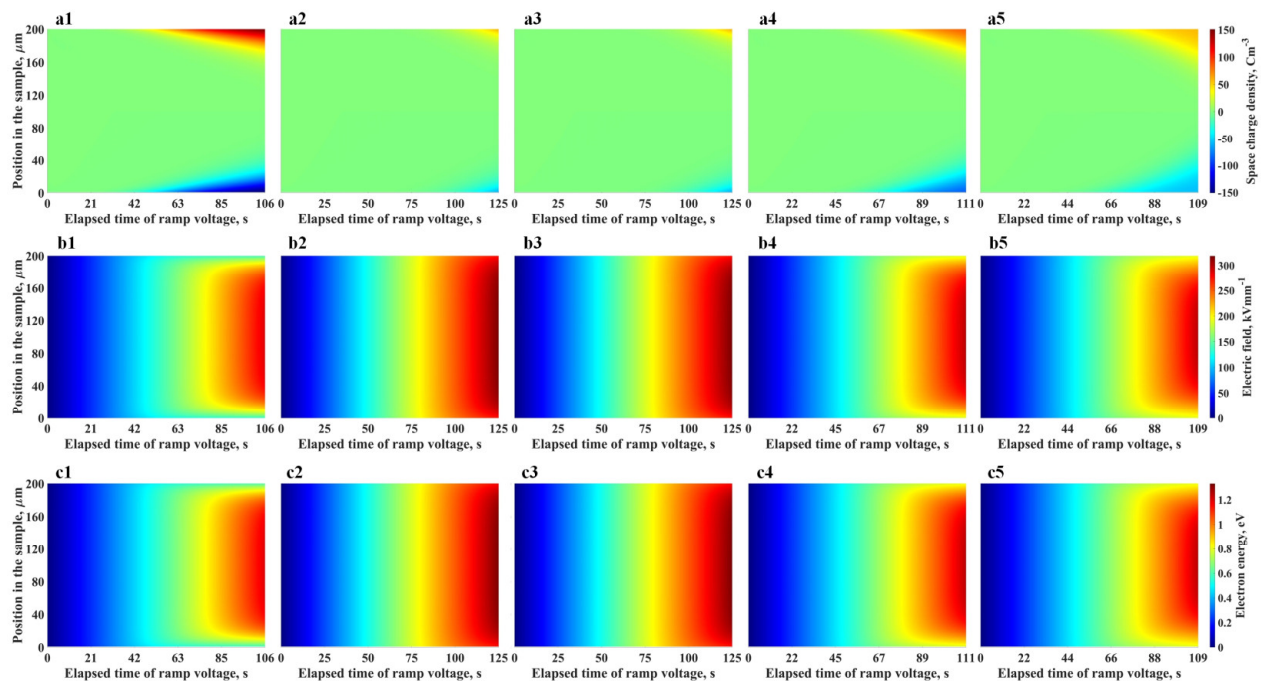


Figure 5. Distributions of space charges (a1–a5), electric fields (b1–b5), and electron energy gains (c1–c5) in pure LDPE and LDPE/Al₂O₃ nanocomposites with nanofiller contents of 0.1 wt%, 0.5 wt%, 2.0 wt%, and 5.0 wt%.

When doped with a small amount of nanofillers, the LDPE/Al₂O₃ nanocomposites produce more traps having deeper energy levels. More homogeneous space charges accumulate near the electrodes, weakening the electric field distortion inside the nanocomposites. In addition, as the traps become deeper, the trapping ability of the deep traps is increased. Two factors work together to increase the breakdown strength of the nanodielectrics having lower nanofiller weight fractions. After doping a large amount of nanofillers, the trap density and energy levels of LDPE/Al₂O₃ nanocomposites decrease due to the overlapping of the interfacial regions. At this time, the electric field in the material is seriously distorted, and the trapping ability of the deep traps is weakened. Their combined effects lead to a decrease in the breakdown electric field of the nanocomposites having larger nanofiller contents.

3.3. Simulation Results of EBMD Model

Figure 6 depicts the variation in the distributions of space charges, electric fields, molecular chain displacements, and electron energies with time in pure LDPE and LDPE/Al₂O₃ nanodielectrics. With the increase in nanofiller content, under the same voltage, the accumulation of space charges in the nanocomposites first decreases and then increases, while the electric field concentration first decreases and then increases. It can be obtained from the dynamic equation of molecular chain motion that, with the increase in nanofiller content, the displacement of molecular chains within nanocomposites first decreases and then increases under the same voltage. This causes the energy accumulated by the electrons to decrease first and then increase. At the same time, it is considered that the trapping ability of deep traps in nanocomposites first increases and then decreases. The energy accumulation of charge carriers in the dynamic free volume and the trapping ability of deep traps together determine the breakdown electric field of nanodielectrics as a function of nanofiller content. With the increase in the mass percentage of nanofillers, the breakdown electric field of the nanodielectrics increased first and then decreased.

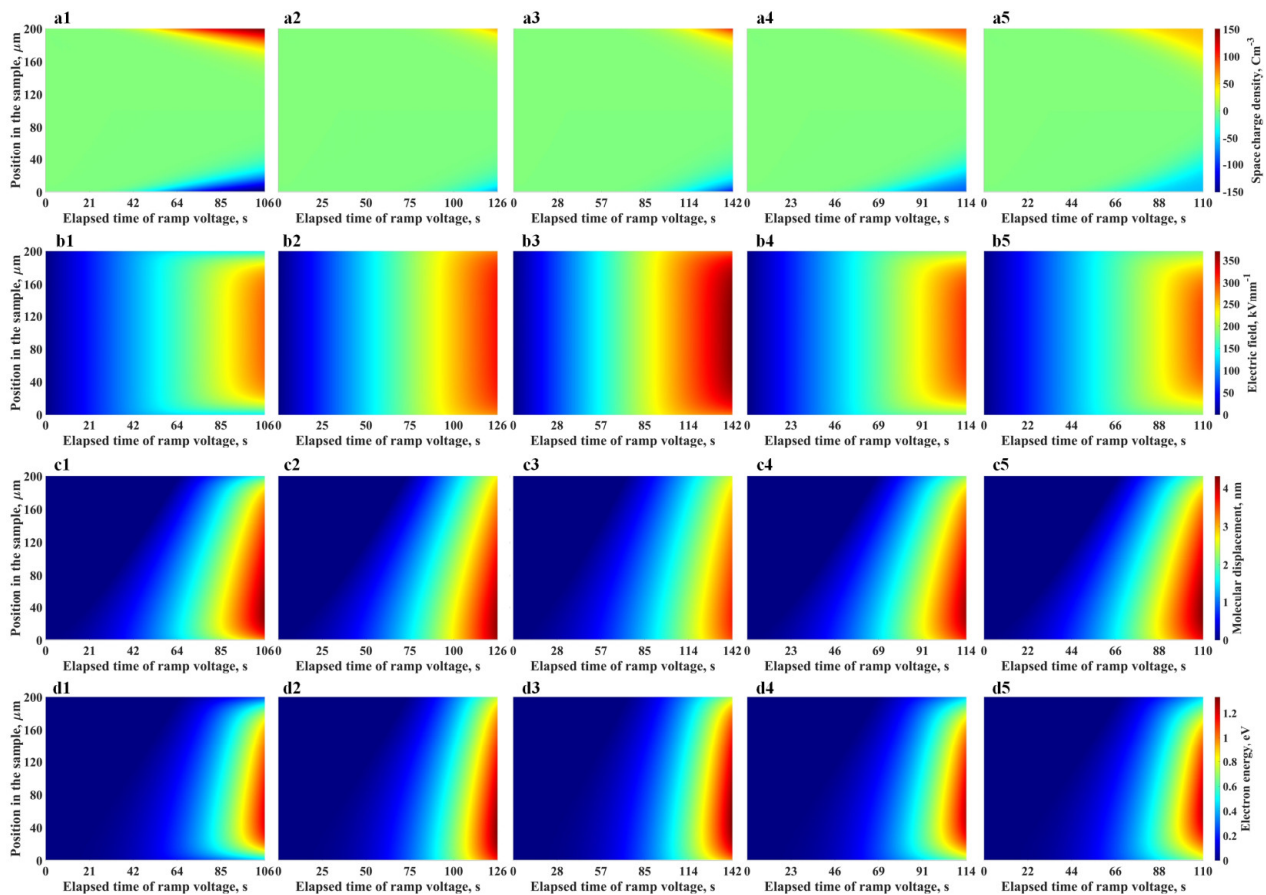


Figure 6. Distributions of space charges (a1–a5), electric fields (b1–b5), molecular displacements (c1–c5), and electron energy gains (d1–d5) in pure LDPE and LDPE/Al₂O₃ nanocomposites with nanofiller contents of 0.1 wt%, 0.5 wt%, 2.0 wt%, and 5.0 wt%.

4. Discussion

In polymer nanocomposites, traps are potential wells formed by polar groups on molecular chains, which can capture mobile charges and then hinder the motion of mobile charges [17,18]. Some of the electrons or holes may be caught in shallow traps and the extended states, and others may be trapped by the deep traps on molecular chains. Free volumes account for some of the space that is not occupied by atoms in polymers. In free volumes, mobile electrons are accelerated. Electrons captured by traps will lead to local space charge accumulation and then distort the local electric field. However, those that are not captured by traps will keep moving, leading to local current multiplication and Joule heating. Nanodoping can change the trap properties and expansion dynamics of free volumes in nanocomposites [20,21]. Figure 7 summarizes the logical block diagrams of EBEF, EBEG, and EBMD models, illustrating the concept of traps and free volumes, and comparing differences among these three criteria.

After charges are injected into the polymer nanocomposites, some mobile charge carriers are captured by deep traps on molecular chains, resulting in the space charge accumulation and electric field distortion. When the highest electric field exceeds a threshold value, namely $E(x,t)_{\max} \geq E_C$ [23], DC electric breakdown occurs, which is the criterion of the EBEF model. The accelerated mobile charges in free volumes that are not captured by deep traps will gain energy from the local electric field. When the highest gained electron energy from the constant scale free volume exceeds the deep trap energy, namely $[e\lambda_0 E(x,t)]_{\max} \geq u_T$ [27], DC electric breakdown occurs, which is the criterion of the EBEG model. The property of interfacial region is extremely vital for the distribution of traps in

the bulk of nanocomposites. Accordingly, the electrical breakdown fields calculated by the EBEF and EBEG models change with the increase in nanofiller contents.

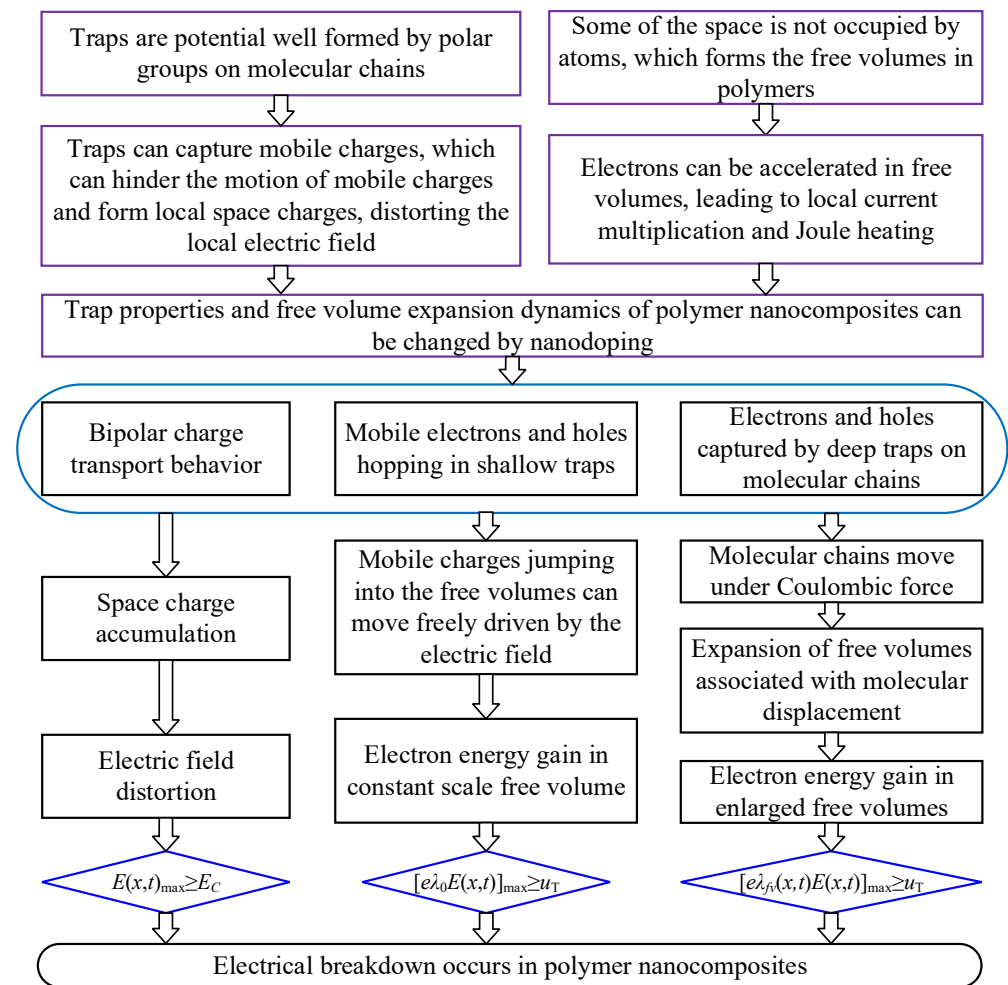


Figure 7. Schematic diagram of EBEF, EBEG, and EBMD models.

With incorporation of different types of nanofiller, the motion behavior of molecular chains also changes. At a relatively low content of nanoparticles, molecular chains are arranged in an orderly manner in interfacial zones. The mean distance between nanoparticles is smaller than the entanglement tube diameter of the polymer with an increase in nanofiller content, leading to continuous overlapping of Gouy–Chapman layers; then, the nanocomposite system changes from polymer-like to network-like [35,36]. In DC electric breakdown experiments, the electric field is sufficiently strong to force molecular chains to move and rotate if they have a dipole moment. Otherwise, the Coulomb force will act on the molecular chains with occupied deep traps and enlarge the local free volume, leading to larger energy accumulation of accelerated electrons. If the electron energy gain in this expanded free volume is higher than the deep trap energy, namely $[e\lambda_{fn}(x,t)E(x,t)]_{\max} > u_T$ [13,25], the electric breakdown may be triggered, which is the criterion of the EBMD model. This model focuses on the molecular chain movement with the deep traps occupied by charges to investigate the influence of charge carrier transport and molecular chain displacement on the DC breakdown strength.

Figure 8 depicts the comparison between the simulated electric breakdown strengths obtained by the three models of EBEF, EBEG, and EBMD and the experimental results of the LDPE/Al₂O₃ nanodielectrics. It demonstrates that, with the increase in nanofiller content, the breakdown strengths obtained by EBEF, EBEG, and EBMD models all show a trend of

increasing first and then decreasing. The general trends of the simulation and experimental results are similar. However, the simulation results of the EBMD model are in best agreement with the experiments. When the nanofiller content is around 0.5 wt%, the simulation results of EBEG and EBEF deviate greatly from the experimental results. According to the experimental results, the maximum electric breakdown strength is 355.8 kVmm^{-1} , which appears at the nanofiller content of 0.5 wt%, while the simulation results of EBEF, EBEG, and EBMD models are 286.3, 312.2, and 356.1 kVmm^{-1} , respectively. It is apparent that the simulation results of the EBMD model are more consistent with the experiments. This indicates that the synergistic effect of deep trap centers in interfacial zones and the tight binding of molecular chains enhance the breakdown performance of LDPE nanocomposites.

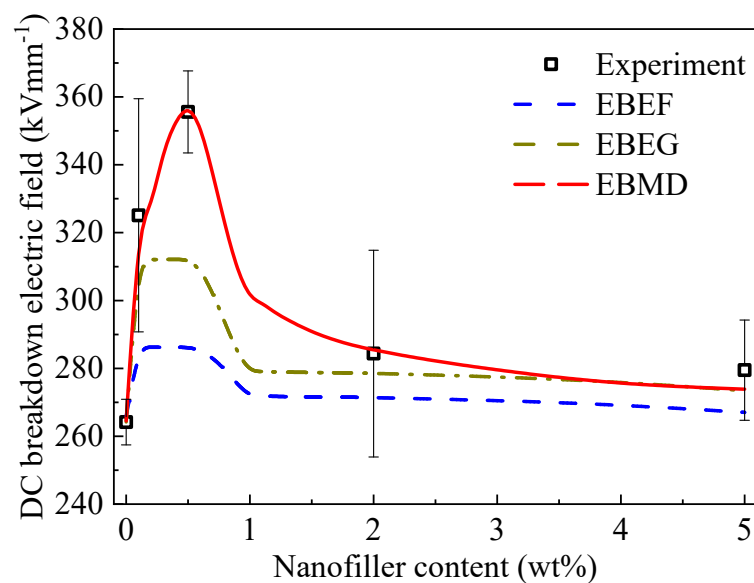


Figure 8. Comparison of EBEF, EBEG, and EBMD simulation electrical breakdown fields with experimental results.

The larger trap energy and density in nanodielectrics doped with small amounts of nanofillers reduce space charge accumulation and electric field concentration, resulting in the increase in the breakdown strength of nanocomposites. However, the changes in trap energy and density have a limited effect on the breakdown electric field. It is necessary to simultaneously consider the space charge accumulation formed by the trapping of deep traps, the free volume expansion caused by the long-range displacement of the molecular chain driven by the electric field force, and the effect of the energy accumulation of electrons in the expanded free volume on the breakdown strength. Comparative studies show that the energy accumulation of electrons in the expanded free volume due to the long-range displacement of the molecular chain dominates the breakdown strength. When the interaction between the molecular chains in the interface region between the nanofiller and the polymer matrix is enhanced, it is difficult for the molecular chains to undergo long-range displacement under the driving of the electric field force. In this case, the free volume expansion is small and it is difficult for electrons to obtain sufficient energy, so the breakdown strength is increased. Therefore, when designing the structure of the interface region, the interaction between the molecular chains in the interface region can be enhanced by the surface modification method, so that the breakdown strength can be greatly improved. LDPE is a key insulating material for power cables and energy storage dielectric capacitors. Revealing the breakdown mechanism of LDPE nanodielectrics can better develop insulating materials with high breakdown strength. This will provide theoretical and simulation model support for the development of high-performance power cables and energy storage dielectric capacitors.

In addition, the aggregated structure of polymer nanocomposites can be changed to some extent, compared to that of pure polymers. The interface between the crystalline region and the amorphous region, and the interface region between the nanofiller and the polymer matrix, may form different trap distributions. The change in crystallinity and the change in lamellar length may change the interaction strength between molecular chains. Because the molecular chains in the interface region are bound by nanoparticles, the interaction strength between the molecular chains also changes. In future studies, we will correlate aggregated structures with trapping effects and molecular chain interactions through density functional theory [37] and molecular dynamics simulations [38]. Then, the EBMD model will be used to determine the effect of the trapping effect and molecular chain interactions on the breakdown strength. Ultimately, a multiscale model will be established to study the relationship among the aggregated structure, the trapping effect and molecular chain interactions, and the electric breakdown performance.

5. Conclusions

The electrical breakdown electric fields simulated by three breakdown models at various nanofiller contents were compared, and the breakdown mechanism of LDPE nanocomposites was illustrated. Doping of Al_2O_3 nanoparticles into LDPE can change the trap, conductivity, and electrical breakdown properties. The results indicated that the charge trapping, molecular motion, and electron energy gain in free volumes are important factors for the electrical breakdown of polyethylene nanocomposites. Then, space charge transport, electron energy gain, and molecular chain long-distance movement were comprehensively considered to investigate the electrical breakdown mechanism of nanocomposites. EBEF, EBEG, and EBMD models were established via focusing on space charge accumulation due to deep trapplings and associated electric field distortion, mobile electrons gaining energy in free volumes, long-distance movement of molecular chains under the Coulomb force expanding free volumes, and accelerating electrons in the enlarged free volumes. Simulation results showed that the EBMD model fits the experimental results much better than the EBEF and EBEG models. The correlation between the long-distance molecular chain movement under the Coulomb force and the electric breakdown characteristics of LDPE was established. The comparisons between simulation results of different models and experiments showed that the electric breakdown electric field of LDPE nanodielectrics is synergistically enhanced by both the strong trapping effect of traps in interfacial regions and the strong binding effect of molecular chains.

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