

Effects of Isothermal Crystallization on Carrier Transport and Breakdown Characteristics of HDPE/LDPE Insulation

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Abstract. In this paper, the influence of the crystalline morphology of high-density polyethylene (HDPE)/low density polyethylene (LDPE) blend on its electrical conductivity, breakdown performance and trap distribution were studied by using the method of isothermal crystallization. Five HDPE/LDPE blends were prepared by melt blending method, and they were cooled to 118°C for isothermal crystallization treatment for 0, 5, 10, 20 and 40 min. The experimental results show that HDPE/LDPE blend with 10min isothermal crystallization time has the lowest conductivity at 70°C, and its conductivity-temperature dependence is also low. As the isothermal crystallization time increases from 0 to 10min, both the DC and AC breakdown strengths of HDPE/LDPE blend increase, and further increase the isothermal crystallization time to 20 and 40min, the breakdown performance of HDPE/LDPE blend decreases significantly. The aggregate structure of HDPE/LDPE blend is closely related to its electrical properties. When the isothermal crystallization time is 10 min, the HDPE/LDPE blend shows a denser crystalline morphology and introduces many of deep traps measured by the isothermal discharge current (IDC) method. Therefore, space charge accumulation and local electric field distortion in the dielectrics are reduced. Also, the breakdown field strength of the HDPE/LDPE blend is improved.

Keywords: Polyethylene, Crystallinity morphology, DC conductivity, Breakdown characteristics, Trap characteristics.

1. Introduction

High Voltage Direct Current (HVDC) transmission is a vital role in global grid interconnection by virtue of its advantages in large capacity and regional grid interconnection [1, 2]. As an important transmission method, HVDC extruded cable power transmission has greater advantages in underground and submarine energy transmission compared to overhead lines [3]. Since the 1960s, cross-linked polyethylene (XLPE) with excellent electrical properties began to be used as medium voltage cable insulation, and has achieved considerable development with the advancement of cable extrusion technology [4, 5]. However, XLPE is a thermosetting polymer, and the insulation cannot be melt-processed again after the cable is retired. Incineration, cracking, burial and other methods not only consume a lot of energy, but also have a great negative impact on the environment [6, 7].

Since the 1950s, thermoplastic polyethylene (PE) has been used for dielectrics and high voltage power cable insulation because of its excellent insulation properties, simple processing technology, and good flexibility [8-11]. The polyethylene commonly used as cable insulation material is divided into high density polyethylene (HDPE) and low-density polyethylene (LDPE). Among them, LDPE has excellent mechanical toughness, but its heat resistance is low. HDPE has a relatively large density, which has higher heat resistance and mechanical strength than LDPE. With the continuous improvement of voltage levels, the electrical, mechanical and thermal properties and long-term stability of a single PE have been difficult to meet the power transmission standards [12]. As a semi-crystalline polymer, PE is composed of crystalline regions and amorphous regions, and its aggregated structure is very critical to its electrical and mechanical characteristics [13]. Blending two or more polymers together by physical mixing means can improve their aggregated structure and obtain more excellent performance [14-16]. Therefore, scholars have turned their research focus to improving the performance of PE through blending modification methods.

Lin et al. found that HDPE acts as a nucleating agent in HDPE/LDPE blends, which significantly reduces the size of spherulites in the blends, which in turn increases the interfacial area between spherulites, and ultimately significantly inhibits the accumulation of space charge [18]. AS Vaughan physically, blended HDPE and LDPE and found that when the mass ratio of HDPE to LDPE is 20:80 and after non-isothermal crystallization with a cooling rate of 0.5-10 K/min, the HDPE/LDPE blend can show better breakdown and high temperature mechanical properties than XLPE. Compared with non-isothermal crystallization, isothermal crystallization at an appropriate temperature can make the crystallization more perfect and show better mechanical properties [18]. Nevertheless, there are few researches on the influence of HDPE/LDPE blend isothermal crystallization on its electrical properties.

In this work, five HDPE/LDPE blends were prepared, and they were cooled to 118°C for isothermal crystallization treatment for 0, 5, 10, 20 and 40 min. Polarized optical microscopy (POM) tests were carried out to characterize the crystalline morphology of HDPE/LDPE blend samples. The DC conductivity, trap energy level distribution, and breakdown strength of HDPE/LDPE blend have been tested. The effects of crystalline morphology of HDPE/LDPE blend on carrier transport and breakdown strength were investigated.

2. Materials preparation and experimental arrangement

2.1 Sample preparation

HDPE/LDPE blend samples were prepared by melt blending method, using 0.9g/cm³ LD100BW low density polyethylene from Beijing Yanshan Petrochemical Company and 0.95g/cm³ L501 high density polyethylene, respectively. In this paper, HDPE/LDPE blend samples with HDPE content of 15 wt % were prepared. The instrument for pressing the sample is the plate vulcanizing machine (JSP-15). The HDPE/LDPE blend was placed in a circular mold at 200 °C at a pressure of 10 MPa for 15 minutes. The temperature was then lowered to 118°C at a rate of 20 °C/min for isothermal crystallization treatment for 0 min, 5 min, 10 min, 20 min and 40 min. The sample was then taken out after cooling to normal temperature. The five samples were named HL-0, HL-5, HL-10, HL-20 and HL-40, respectively.

2.2 Crystallinity morphology

POM (BX51, Olympus, Japan) was used to obtain crystallinity morphology of HDPE/LDPE blend and to observe the effect of IC time on crystal morphology. A thin film of about 30μm was prepared. A round sample of 10mm diameter was cut out and placed under POM. The temperature control conditions are the same as the one used for sample preparation. It has a precision melting point meter.

2.3 DC conductivity

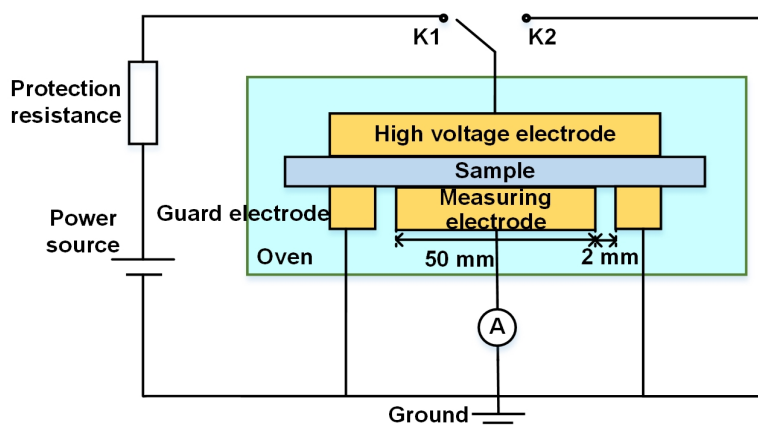


Fig. 1 Schematic diagram of the DC conductivity test.

DC conductivity was measured by three-electrode method at 30°C, 50°C and 70°C under an electric field of 20 kV/mm [19]. Schematic diagram is shown in Figure 2 (Connect the switch to K1). Electrode material is aluminum. The measuring electrode's and the ring electrode's diameters are 50mm and 60mm respectively.

2.4 Isothermal discharge current

Isothermal discharge current (IDC) test was conducted in order to calculate the trap level distribution of HDPE/LDPE blend [14]. Schematic diagram of the IDC experiment is shown in Figure 1. A a thickness of $300 \pm 10 \mu\text{m}$ sample was polarized at 30 kV/mm at 50°C for 40 min (Connect the switch to K1). Then, an electrometer (Keithley 6517B) was used to quickly short-circuit both sides of the sample for 40 min to collect depolarizing current (Connect the switch to K2). The trap energy (E_t) and density ($N_t(E_t)$) in the dielectric can be calculated by [20]:

$$N_t(E_t) = \frac{2dIt}{el^2k_B T} \quad (1)$$

$$E_t = k_B T \ln(vt) \quad (2)$$

Where d represents specimens' thickness and l is charges injection depth. e is the standard charge amount. k_B is the Boltzmann's constant. T is the absolute temperature. v represents the escape frequency of trapped charges.

2.5 DC breakdown strength

It was measured by the spherical electrode method in transformer oil at 30°C to prevent air discharge and arcs. Figure 2 is a schematic diagram of the experimental apparatus. The whole experimental system includes: 50kV high-voltage DC power supply, protection resistance, stainless steel spherical electrode, AC and DC resistor-capacitor voltage dividers ($R1: R2 = 1:1000$), etc. The electrode material is aluminum. The spherical electrode's diameter is 25mm. A $85 \mu\text{m}$ -thick sample was placed between the spherical electrode. The flat electrode is at a rate of 500 V/s until the sample breaks down. Each sample was repeated for 15 times. The breakdown results are analyzed by the Weibull distribution [21, 22].

$$P(E_b; \alpha, \beta) = 1 - \exp \left[- \left(\frac{E_b}{\alpha} \right)^\beta \right] \quad (3)$$

$$P(i; n) = \frac{i - 0.44}{n + 0.25} \times 100\% \quad (4)$$

Where E_b is the breakdown strength that can be obtained from the experiment, P is the breakdown probability when the breakdown voltage is less than or equal to the breakdown voltage, and α is the breakdown strength when the breakdown probability is 0.632. E is the characteristic breakdown intensity and β is the shape distribution parameter representing the dispersion of breakdown results. The larger the β , the smaller the breakdown voltage range and the better the dispersion of the measured data.

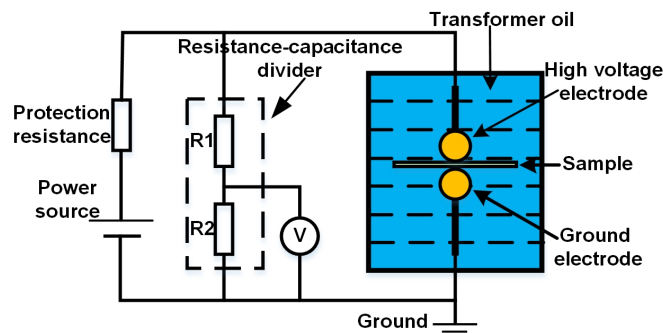


Fig. 2 Schematic diagram of the DC conductivity test.

3. Experimental results

3.1 Characterization of crystallinity morphology

Polyethylene is a semi-crystalline polymer, its aggregated structure is related to the electrical properties of the polymer, such as crystal size and internal defects will affect the insulation properties of polyethylene [14, 23]. In this paper, the crystalline morphology of HDPE/LDPE blend is controlled by isothermal crystallization method.

Figure 3 is the crystalline morphology of HDPE/LDPE blend. After the HDPE/LDPE blend is heated to 200°C, part of the crystal nucleus can be observed as shown in Figure 3a, and the spherulites will grow centered on the crystal nucleus. When the HDPE/LDPE blend is cooled from 200°C to normal temperature at a rate of 20°C/min, its crystalline morphology is imperfect, and there are a large number of fragmental crystals in the POM as shown in Figure 3b. When the HDPE/LDPE blend is crystallized isothermally at 118°C for 5 min and then cooled to normal temperature, its crystalline morphology becomes perfect, but there are still a small amount of fragmental crystals as shown in Figure 3c. As shown in Figure 3b, when the isothermal crystallization time is increased to 10 min, the spherulites of HDPE/LDPE blend have sufficient time to grow, and the spherulites are densely connected. When the isothermal crystallization time is further increased to 20 min, the size of the spherulites becomes larger, and a large amount of free volume exists between the spherulites as shown in Figure 3e. When the isothermal crystallization time is increased to 40 min, the size of the spherulites and the free volume between the spherulites have increased significantly as shown in Figure 3f, which is vidently harmful to the electrical properties of the polymer dielectrics [24].

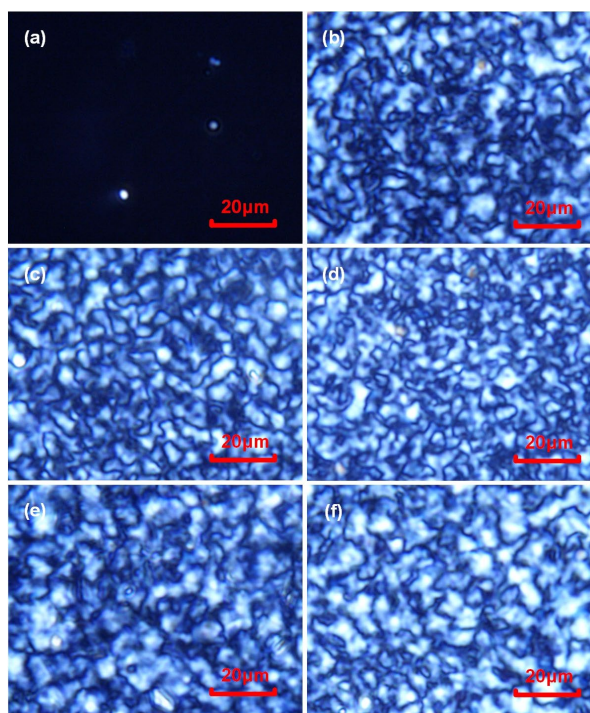


Fig. 3 POM images of HDPE/LDPE blend.

3.2 DC conductivity

Figure 4 depicts the DC conductivity under 30°C, 50°C and 70 °C of HDPE/LDPE blend. It can be seen that as the temperature rises from 30 to 70°C, the conductivity of HDPE/LDPE blend has increased significantly. As the isothermal crystallization time increases from 0 to 40 min, the conductivity of HDPE/LDPE blend first decreases and then increases. Among the five samples, HL-0 showed the highest conductivity. Its conductivity at 30, 50 and 70°C was 1.29×10^{-15} , 2.21×10^{-14} and 2.25×10^{-13} , respectively. In addition, HL-10 has the lowest conductivity at 70°C, which is 1.31×10^{-13} .

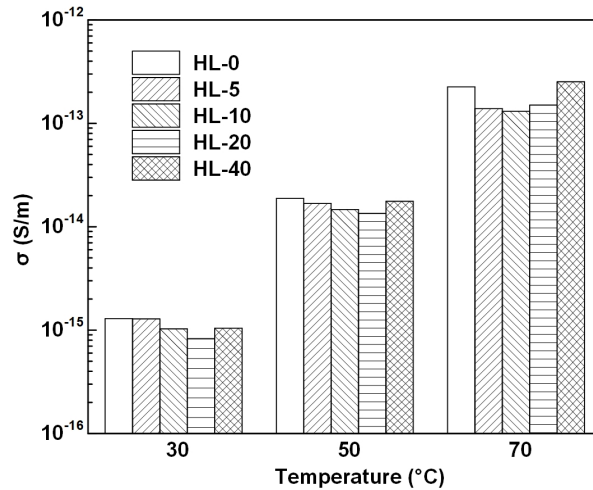


Fig. 4 DC conductivity of HDPE/LDPE blend.

The electric field distribution control of HVDC cables will become a key issue in the design and operation and maintenance of DC cables [25]. During the operation of DC cables, because of the existence of temperature gradient in the insulation layer and the negative temperature coefficient of the insulation material resistivity, the electric field distribution in the insulation layer will be reversed, which will increase the difficulty of the DC cable insulation structure design [26]. Therefore, the influence of the resistivity of the insulating material with the temperature change must be considered in the design of the DC cable insulation [25]. Their relationship is [27]:

$$\sigma = A \exp\left(-\frac{E_\tau}{kT}\right) \frac{\sinh(B|E|)}{|E|} \quad (5)$$

Where σ represents the conductivity; A and B are constants; E_τ is the conductivity activation energy; k is the Boltzmann constant; T is the absolute temperature; E is the electric field strength. Take the logarithm of both sides of the Eq. (5) to get the following equation:

$$\ln \sigma = \ln \frac{A \sinh(B|E|)}{|E|} - \frac{E_\tau}{kT} \quad (6)$$

The logarithm of the conductivity and the absolute temperature is shown in Figure 5. It is obvious that HL-5 and HL-10 have lower conductivity activation energies, which are 1.05 and 1.08 eV, respectively. Thus, the conductivity-temperature dependence of HL-5 and HL-10 is low, which is beneficial for homogenizing the electric field distribution of HVDC cables.

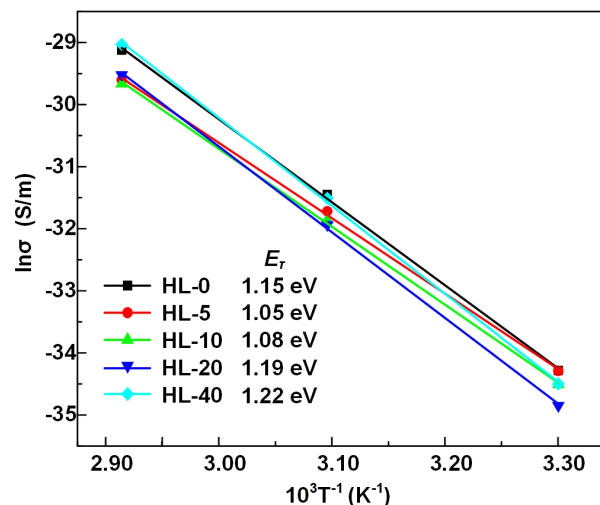


Fig. 5 Relationship between logarithm of the DC conductivity under 20 kV/mm and the reciprocal of the absolute temperature. E_τ is conductivity activation energy.

3.3 Breakdown strength

Figure 6 exhibits the two-parameter weibull distribution of the DC and AC breakdown strength at 30°C for HDPE/LDPE blend. E_{dc} and E_{ac} are the measured DC and AC field strengths at which there is a 63.2% probability for the samples to breakdown. As the isothermal crystallization time increases from 0 to 10min, both the DC and AC breakdown strengths of HDPE/LDPE blend increase, and further increase the isothermal crystallization time to 20 and 40min, the breakdown performance of HDPE/LDPE blend decreases significantly. It can be clearly seen that the E_{dc} and E_{ac} of HL-10 are both the highest, which are 409.8 and 226.1 kV/mm, respectively. Compared with HL-0, the DC and AC breakdown strengths of HL-10 are increased by 15.5% and 28.7%, respectively. In addition, the breakdown strength of HL-20 and HL-40 has greater dispersion, which may be due to the free volume between the larger spherulites as shown in Figure 3 (e-f).

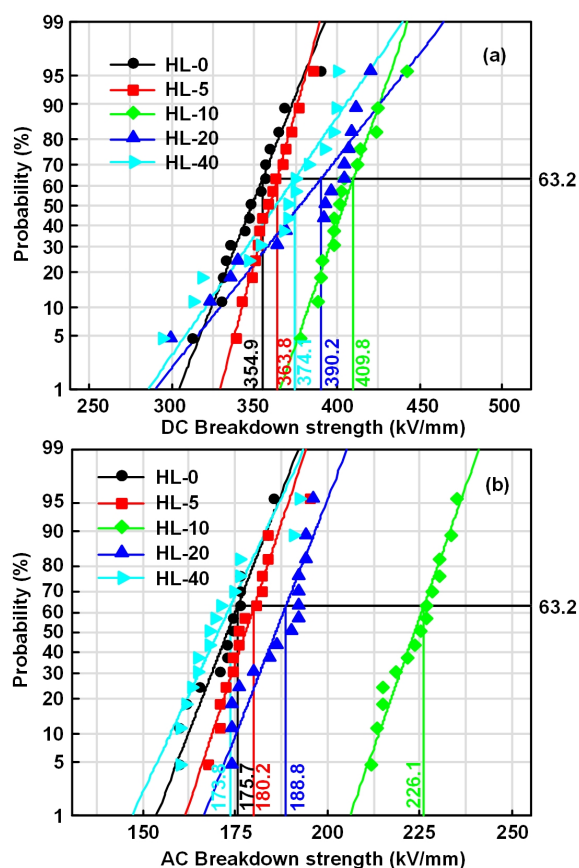


Fig. 6 DC (a) and AC (b) breakdown strength of HDPE/LDPE blend.

4. Experimental results

4.1 Effect of crystalline morphology on carrier transport

Polymers have a complex aggregation structure, so there are many localized states that can capture charges in the band structure of the material, and they are called traps. The trap distribution measured by the IDC method in this paper is shown in Figure 7. Levels are deep trap energy are 0.980, 0.986, 0.988, 0.987, 0.983eV, respectively. Figure 8 shows the relationship between deep and shallow trap densities and isothermal crystallization time of HDPE/LDPE blend. As the isothermal crystallization time increases from 0 to 10 min, the deep trap density of HDPE/LDPE blend increases. When the isothermal crystallization time further increases to 40 and 100 min, the deep trap density of HDPE/LDPE blend decreases significantly. The shallow trap density also shows a similar trend to deep traps. The deep trap and shallow trap densities of HL-10 both reached their maximum values of 6.3×10^{20} and 5.3×10^{20} eV⁻¹/m³, respectively.

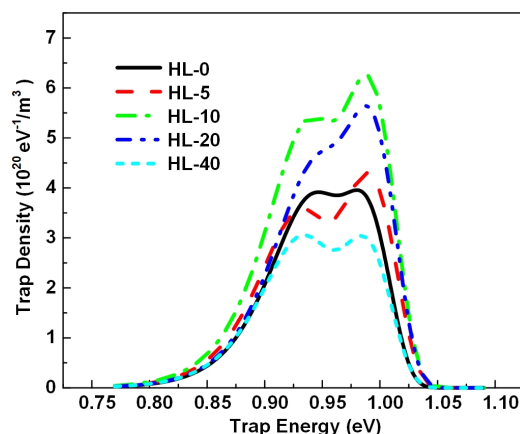


Fig. 7 Trap level distribution of HDPE/LDPE blend.

The trap energy level distribution of HDPE/LDPE blend is closely related to its aggregate structure. When the isothermal crystallization time of HDPE/LDPE blend is 0 and 5 min, the lamellae do not have sufficient time to stack to form perfect spherulites, resulting in weaker connection between the fragmental crystals. Therefore, the trap energy level and HL-0 and HL-10's density are lower. When the isothermal crystallization time of HDPE/LDPE blend is increased to 10 min, the coupling force between the perfect spherulites becomes larger and the gap between the spherulites decreases, which is conducive to the formation of more deep traps. When the temperature crystallization time is increased to 20 min and 40 min, the lamellae stack forms large-size spherulites, and there is a large amount of free volume between the spherulites, which results in a decrease in the density of deep traps.

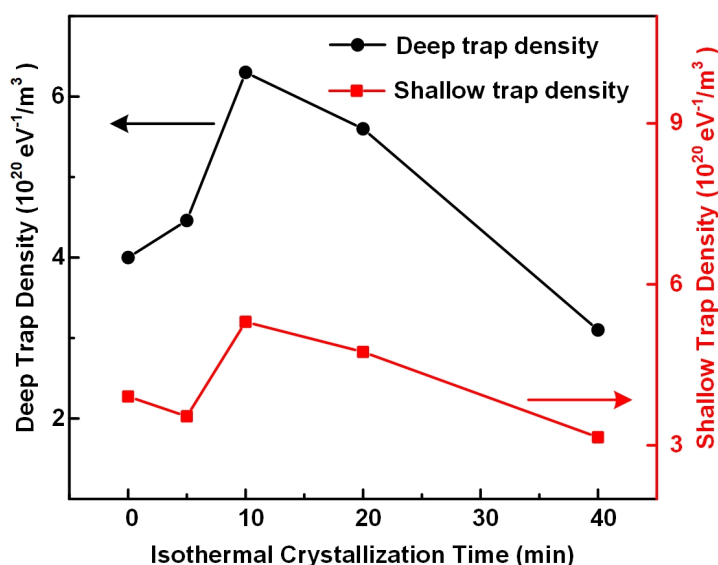


Fig. 8 Relationship between deep and shallow trap densities and isothermal crystallization time of HDPE/LDPE blend.

The trapping effect of deep traps on carriers is very obvious, which is very important for studying the transport of carriers. On the one hand, the higher the energy level of deep traps, the greater the energy required for carrier detrapping. On the other hand, the increase in the density of deep traps can strengthen the trapping effect of charges, reduce the mobility of carriers, and thus reduce the conductivity. The deep trap density of HL-0 and HL-5 is lower, and carriers are more easily transported in the free volume between the fragmented crystals, so their conductivity is higher. HL-10 and HL-20 have relatively dense crystalline morphology. Many deep traps can effectively capture carriers, thereby significantly reducing its electrical conductivity at high temperatures. The deep traps density in HL-40 is reduced, and carriers are more easily transported under electric field, resulting in higher conductivity.

4.2 Effects of trap distributions on breakdown strength

The aggregate structure formed by the coupling of its crystalline and amorphous regions is a key factor affecting its macroscopic electrical and mechanical properties. The crystalline region is composed of independent lamellae or spherulites composed of lamellae radially. The deep traps in the dielectric body mainly come from the interface area between the spherulites.

As shown in Figure 9, DC and AC breakdown strength and the deep trap density of HDPE/LDPE blend is described. The symbols in the figure are the actual test results, and the curves are obtained by fitting. In general, the DC and AC breakdown strength of HDPE/LDPE blends increase significantly as the density of deep traps increases. It is obvious that HL-10 has the highest trap density, and its DC and AC breakdown strength is also the highest.

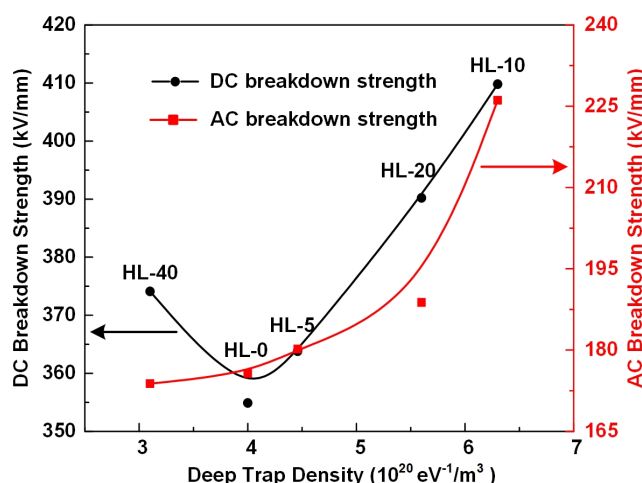


Fig. 9 Relationship between breakdown strength and deep trap density HDPE/LDPE blend.

The mechanism by which the density of deep traps affects the breakdown strength of HDPE/LDPE blend can be summarized in the following two points: Firstly, the increase in deep traps density strengthens the capture of charges and reduces the mean free path and mobility of carriers. Therefore, the collision ionization behavior of carriers is suppressed, and the breakdown field strength is increased. Additionally, the injected charge near the electrode can be captured by the deep trap, thereby forming homopolar space charges, which inhibits the charge injection electric field near the electrode. Therefore, the space charge accumulation and local electric field distortion in the dielectric are reduced, and finally the breakdown field strength of the HDPE/LDPE blend is improved.

5. Conclusion

The HDPE/LDPE blend is cooled to 118°C for isothermal crystallization treatment for 10 min, which can effectively improve its crystalline morphology, and the connection between spherulites will be closer, thereby increasing the density of deep traps. In addition, HL-10 is at 70 °C conductivity is also significantly reduced, which is helpful for homogenizing electric field distribution of HVDC cables. The increase of deep trap density is beneficial to enhance the breakdown strength of HDPE/LDPE blend, the most obvious is that HL-10 has the highest trap density, and its DC and AC breakdown strength is also the highest. However, the mechanical properties of HDPE/LDPE blends need to be improved, and more research is needed to further improve their mechanical properties.

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