International Research Journal of Infinite Innovations in Engineering and Technology (IJIIET) ISSN: 2349-2287
Vol.4, Issue No 2, 2024

Tailoring Polymeric Insulation Materials for DC Cable Dielectrics

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Abstract—

Chemical and physical defects are thought to be responsible for trapping of charge carriers in polymeric insulating materials such as crosslinked polyethylene (XLPE). The present work aims at increasing the basic understanding of the effect of physical defects on charge transport. In this paper, two insulating XLPE materials, used in DC and AC high voltage cables, were studied. The results show that DC-XLPE has a relatively lower activation energy than AC-XLPE. The mechanism for reducing the activation energy from physical defect point of view is discussed. A framework leveraged on Anderson localization was developed to elucidate the contribution of localized states due to physical disorder in lowering the activation energy of conductivity. Furthermore, the density functional theory (DFT) computations have been carried out to study the impacts of disorder on PE by copolymerization with different comonomers on the electronic structure. By copolymerizing the PE with various comonomers, more localized states were observed making the physical disorder become more dominant thus the properties of PE can be tailored.

Keywords—direct current (DC); cable insulation; activation energy; conductivity; copolymerization.

INTRODUCTION

The increasing penetration of renewable energy in the traditional power system and particularly the massive integration of offshore wind farms calls for the ever increasing deployment of DC cabling [1,2]. DC insulation design is more of fundamental science than engineering development. Technical publication usually describes experimental studies on the electrical properties of different cable insulation compounds. However, the processing of polymer compounds during cable production has a significant influence on the morphology and thus the electrical properties. For instance, the morphology of crosslinked polyethylene may vary depending on specific manufacturing processes. The model developed in [3] provides a basis for the proper balance between key electrical properties of DC insulation. The focus there was to develop a relatively simple formalism which includes the correlation between the conductivity and space charge based on two physical parameters, activation energy (ξ) and mean trap separation (λ). The effect of activation energy on the field grading behavior was discussed, and a summary of optimum design space was presented based on two design constrains (power density and Field Enhancement Factor). The focus of this paper is on the mechanisms of controlling the DC conductivity in polymer when the crystalline order is disturbed. A framework leveraged on Anderson localization was developed to clarify the contribution of localized states due to physical disorder in controlling the activation energy and the temperature coefficient of conductivity.

EXPERIMENTAL AND COMPUTATIONAL INVESTIGATION

Two kinds of cross linkable polyethylene compounds were characterized. One was the XLPE used in HVDC cable and the other used in HVAC cable. The samples were prepared from commercial pellets by hot pressing. Before any electrical measurement, thin slab samples were degassed for five days at 80oC in vacuum. The DC conductivity of plaque specimens were measured using a three-terminal sample holder which was designed according to ASTM 257 specifications. Crystallinity was calculated from the results of solid-state NMR experiment conducted at room temperature on a Bruker Avance III 100 MHz Wide Bore (WB) NMR spectrometer (0.94 T field), with a 13C resonance frequency of 25.152 MHz. The samples were placed in a static zirconia rotor-oriented MAS to the field. The pulse sequence used for this experiment is the common cross-polarization sequence with an 8.5-/us 90° pulse, a 1-ms contact time, a 40-ms acquisition time.

DFT computations were performed using the vasp package [4], with the Perdew-Burke-Ernzerhof (PBE) XC functional [5] and a plane-wave energy cutoff of 400 eV. Monkhorst-Pack kpoint meshes of 2×1×1 and 1 ×1 ×1 were applied for PE with chemical and physical defects, respectively. All structures generated by classical molecular dynamics (MD) were fully relaxed using the PBE functional and then used to compute the electronic structure with the HSE06 functional. In these calculations, the vdW-DF2 functional was adopted to improve the van der Waals interactions [6]. Classical MD simulations were carried out in the LAMMPS simulation package, with the OPLS-AA [7] force field and a time-step of 1 fs. III. SIGNIFICANCE OF ACTIVATION ENERGY FOR DC CABLE Temperature-dependent conductivity is often characterized by the activation energy and can be estimated using the slope of the

Arrhenius plot with a simple exponential fitting function [8,9]

$$\sigma(T) = \sigma_0 \exp\left(\frac{-\xi q}{k_B T}\right) \qquad (1)$$

where σ0 is the conductivity at reference temperature (S/m), ξ is the thermal activation energy (eV), q is the electronic charge (C), kB is the Boltzmann's constant (J/K), T is the absolute temperature (K).

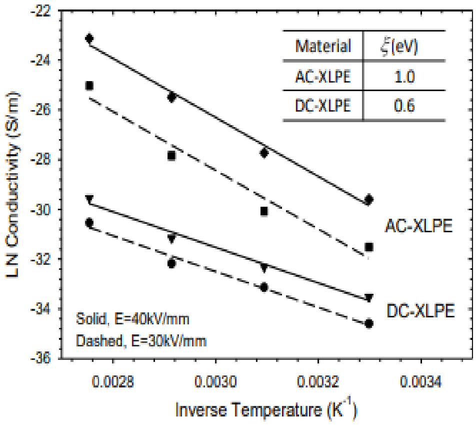

Fig. 1. Arrhenius plots for the conductivities of AC-XLPE and DC-XLPE at 30 kV/mm and 40 kV/mm on temperature range 30oC - 90oC. Fig. 1 shows the Arrhenius plots of the DC conductivity, extracted from the quasi steady-state current measurement at 30 kV/mm and 40 kV/mm. From the slopes of the fitted curves, an activation energy is obtained corresponding to the effective trap depth (i.e., thermally activated hopping). As can be seen from Fig. 1, the conductivity of DC-XLPE and AC-XLPE increase exponentially with the increase of temperature. AC-XLPE has a higher electrical conductivity than that of DC-XLPE. The activation energies are ~ 1.0 eV for AC-XLPE and ~0.6 eV for DC-XLPE, respectively.

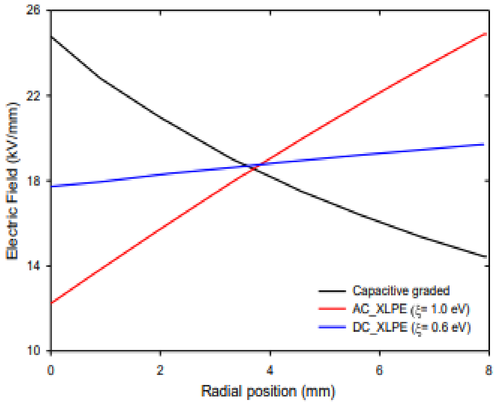

Fig. 2. A demonstration of the effect of activation energy in DC cable. All curves were computed for a conductor temperature of 70 oC and a ground temperature of 55 oC.

The significance of activation energy for DC cable insulation can be demonstrated by solving the electric field distribution for a cable with 11 mm radius conductor and 8 mm wall dielectric, operated at 150 kV with an average field of 18.75 kV/mm under load conditions [8]. For the case of AC-XLPE with high temperature coefficient (0.98 eV), the field at the ground shield is 25 kV/mm. This is a undesirable configuration which makes inefficient use of the dielectric insulation. With the activation energy reduced to 0.6 eV (DC-XLPE), the field is nearly uniform radially across the cable insulation with the ground shield field at only 19.8 kV/mm under DC grading. Based on the above discussion, one can appreciate why a low activation energy materials is favorable for DC cable. The real question here would be, what is the mechanism behind the reduction in the activation energy from 1 eV to 0.6 eV? How can we relate the activation energy to the morphology, chemical structure and molecular motion of the system? The subject of the next section is to form a framework to address such key and challenging question.

MECHANISM FOR REDUCING ACTIVATION ENERGY

Disorder induced localization:

Hopping conduction through localized state It is well-known that the DC conductivity are highly dependent on chemical defects [10,11]. However, the potential effect of physical defect caused by morphological, conformational or density deviations from the perfect crystalline PE structure on DC conductivity is not understood. P.W. Anderson's localization theory for the electrical properties of amorphous materials postulates localized states in forbidden band in addition to extended states above the mobility edge [12]. Under low field and at low temperature, carriers can only transport between these localized states through hopping or tunneling [12,13]. Generally, introducing the disorder in an insulating material leads to the formation of localized electronic states i.e., Anderson localization. States due to structural disorder are mainly localized in the band tail whereas chemical defects give rise to deep impurity states [14]. Assuming a parabolic distribution, the density of states N(E) is given by [14],

$$N(E) = \frac{\sqrt{2}}{\pi^2}\left(\frac{qm^*}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \qquad (2)$$

where N(E) is the density of states in the conduction band, m* is the effective electron mass, h is plank constant and E is the energy of states. The number of localized states per unit volume, Nc can be calculated by

where Ec is the mobility edge.

$$N_c = \int_0^{E_c} N(E)dE = \frac{2\sqrt{2}}{3\pi^2}\left(\frac{qm^*}{h^2}\right)^{\frac{3}{2}} E^{\frac{3}{2}} \qquad (3)$$

The energy bandwidth of localized states in conduction and valence band tails depends on the degree of disorder, Nc/N, where N and Nc are the number of atoms and the number of localized states per unit volume, respectively. With low disorder, conduction is mainly due to extended states, whereas under high disorder the conduction is hopping through localized states [10].

In the seminal work by G. Blaise [10], the mobility in the localized states of the conduction band is given by,

$$\mu = 2.4\times10^{-9}\,\frac{W(E_c)N_c^{\frac{1}{3}}E_c^{\frac{3}{2}}}{N(E_c)(k_BT)^{\frac{9}{2}}}\,e^{-2\alpha R_c}\,e^{-W(E_c)/k_BT} \qquad (4)$$

where μ is the mobility, W(Ec) is the activation energy at mobility edge, Nc is the localized states, Ec is the mobility edge, α is the extension of wave function which ranges 0.4-0.5 nm, Rc is the average distance between localized states. Assuming each of the localized states are centered at a cube whose volume is (2RC) 3 then Rc=0.5Nc 1/3 [10]. Eq. (4) contains an activation energy at the mobility edge W(Ec) which characterized the hopping conductivity. The measured activation energy ξ of the thermally activated hopping mobility in band tail states is usually obtained by using an expression of the form,

$$\mu = \mu_0 \exp\left(\frac{-\xi}{k_BT}\right) \qquad (5)$$

where the pre-exponential term μ0 is a constant that has been interpreted in different ways by various authors, both in a classical [10] and a quantum mechanical approach [11]. Here we consider μ0 = 0.024 m2 /V s according to D K Davis [12]. We can drive an expression for the activation energy ξ by equating the experimentally determined thermally activated hopping mobility equation (5) and the theoretically derived average mobility in the localized states of the conduction band equations (4) at different temperatures. From the calculation of the temperature dependence of the mobility the activation energy is plotted as shown in Fig. 3. It is interesting to see when the number of localized states increased (degree of disorder is increased), the activation energy is reduced. So, what degree of disorder (localized states) has to be introduced to achieve the desirable design space (ξ=0.4-0.5eV) for DC cables? This is shown by the blue lines. The degree of disorder should be in the range of 0.015 (Nc=1E21 cm-3). The most important point is that localized states do guarantee that the system will have a lower activation energy (or lower conductivity) than the ordered counterpart, due to the introduction of physical disorder

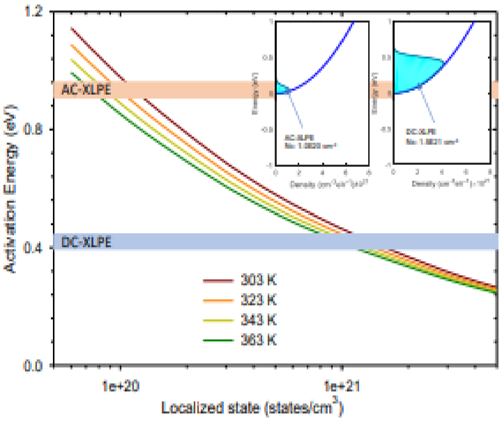

Fig. 3. Activation energy as function of disorder. The activation energy can be controlled by increasing the density of localized states. The activation energy for optimal DC insulation (0.4-0.5eV) can be achieved with a Nc=1E21 cm-3 . The inset shows the density localized states (shaded area) calculated according to eq (3).

Crystallinity from static solid state NMR spectra

The main differences between crystalline and amorphous phases are attributed to the order and disorder of polymer chains. In the crystalline phase, polyethylene takes the all transzigzag conformation, while, in the amorphous phase, a rapid transition between the trans and gauche conformations takes place. The crystallinity of AC-XLPE and DC-XLPE are determined by fitting the spectrum with two different chemical shielding tensors, corresponding to the two different phases in the sample as shown in Fig. 4. One tensor represents the crystalline phase and one represents the amorphous phase. The ratio of the integrated crystalline tensor to the total integral (amorphous + crystalline) is taken as a good estimate of the crystallinity. The dmfit program was used to calculate the best fit spectrum from the measured solid-state, 1H-decoupled, CP static 13C NMR spectrum by varying parameters until the sum of squares of deviations between the measured spectrum and the calculated spectrum is minimized [13,14]. The calculated crystallinities of AC-XLPE and DC-XLPE are 43.3% and 31.8% respectively, which shows DC-XLPE is more disordered than

AC-XLPE. Further study is on-going for thorough understanding of the contribution of the trans and gauch confirmations to the overall confirmation of polyethylene.

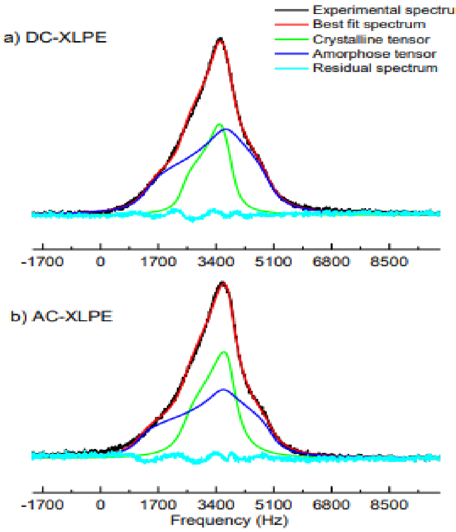

Fig. 4. Cross-polarized, 1H decoupled, static, 100 MHz 13C NMR spectrum of a) DC-XLPE b) AC-XLPE. Experimental spectrum (Black curve), Calculated best-fit spectrum, the sum of the crystalline and the amorphous tensor components (Red curve). The crystalline tensor (Green curve). The amorphous tensor (Blue curve). Residual spectrum (Cyan=Black Curve-Red curve).

DENSITY FUNCTIONAL THEORY CALCULATION

To further validate the above argument, additional DFT calculations have been carried out to study the impacts of disorder on PE. The structure of pure PE with different comonomers including 1,7-octadiene, 1,9-decadiene and 1,13- tetradecadiene were generated from a single PE chain with 302 atoms. Two-step MD ensemble simulations were used: 1) NVT ensemble, PE structures were simulated at T=600 over 1 ns, followed by a cooling procedure from 600 K to 300 K over 1 ns, and further equilibrated at 300 K over 1 ns; 2) NPT ensemble, P= 1 atm along two directions was performed on the resulting structures for 5 ns to generate the polymer slabs [19]. From Fig. 5, we note that different levels of gauche defects (CCCC torsion angle closing to 60/120 degree, with respect to 0/180 for perfect chains) present in PE due to joins between the copolymers and the main PE chains. Such physical defects can degrade the electronic structure by extending the conduction and valence band tails, as shown in Fig. 5. The resulting electron trap depth ranges from 0.3 to 0.5 eV, being close to the measured activation energy of DC-XLPE (0.6 eV). These findings indicate that our argument of introducing physical defect (i.e., gauche defects) to lower activation energy is plausible.

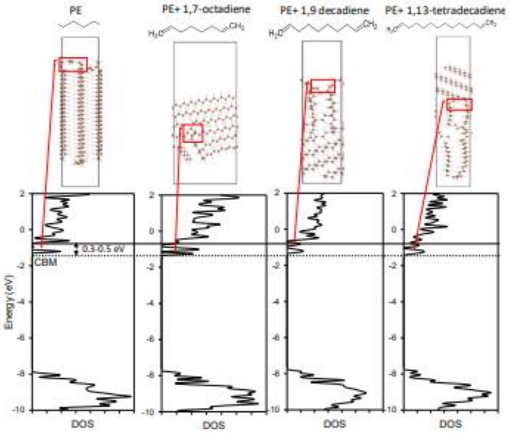

Fig. 5. (Top) Physical structures of PE with different cross-link groups (1,7- octadiene, 1,9-decadiene and 1,13-tetradecadiene), generated by MD simulations. (Bottom) Corresponding density of states (DOS) of PE.

CONCLUDING REMARKS

In this article, we tried to emphasize how the electrical performance of PE is influenced by its shape. In order to clarify the role of localized states resulting from physical disorder in lowering the activation energy of the conductivity, a framework based on Anderson localization was devised. One can imagine the Anderson localized energy states being connected to structural diseases (gauche conformations). Enhancing physical disorder by copolymerizing the PE with different comonomers causes differing degrees of disorder in potential wells and subsequently more localized states. When this increased physical disorder is properly calibrated, it produces activation energy adequate for DC-XLPE.

As a result, the properties of PE can be modified, resulting in the acquisition of more desirable features for the design of extrudable polymeric materials in the future for DC cable applications. Such a mechanism is thought to be responsible for the effective development of DC-XLPE. However, the framework must be strengthened by quantitative metrics from the perspectives of physical, material, chemical, and computational factors.

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