E-FIELD DEPENDENT CONDUCTION IN LOW-DENSITY POLYETHYLENE

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Abstract

Measurements of the resistivity of low density polyethylene (LDPE) samples of varying thickness have been made using the standard constant voltage method to explore electric field dependence using conduction mechanisms developed for amorphous solids and semi-conductors. Resistivity is related to carrier mobility within the bulk. Where electrons are the primary charge carriers, their mobility is dependent on their probability of hopping between trapping sites treated as potential wells. A series of constant voltage measurements at constant temperature show that LDPE follows the Poole-Frenkel theory of field-enhanced conduction at low applied fields.

Introduction

High resistivity insulating polymers are ubiquitous in use, easily tailored to address specific chemical requirements, and endless in their possible applications in new technology. The prevalence of these materials in the design of spacecraft components places special emphasis on the electrical properties of the insulators, which are critical for anticipating and preventing potentially damaging spacecraft charging phenomena [1,2].

Electrical properties of insulators are significantly different from the electrical properties of conductors and semi-conductors, both experimentally and in the fundamental understanding of their behavior. The most promising theoretical possibilities for explaining electrical behavior in insulating polymers are concepts and models that have proven successful in application to semi-conductors and amorphous solids [3,4].

The conductivity of the material, and the resistivity by $\sigma = 1/\rho$, is the relevant property for determining mobility of charge carriers and dissipation rate of accumulated charge within the material. These theories are well tested for semi-conductors but remain largely unverified for insulators [5].

Fundamental assumptions of conductivity models applied to semi-conductors include the identification of electrons or holes as the primary charge carriers. Their motion through the material is governed by availability of localized states treated as potential wells in the lattice, as illustrated in Fig. 1.

Fig. 1 Representation of carrier motion by way of hopping between potential wells. ΔH and a correspond to structural elements of the material [4,5].

The electron, or hole, moves through the material by hopping between these localized states or traps. Energy is required to release the carrier from the trap and the conductivity is proportional to the probability that hopping will occur [3,4]. The hopping conductivity is dependent on carrier mobility, which is influenced by both temperature and applied electric field. In general,

$$\sigma_{hop}(E,T) = \left[\frac{2 \cdot n(T) \cdot \nu \cdot a \cdot e}{E}\right] \exp\left[\frac{-\Delta H}{k_B \cdot T}\right] \sinh\left[\frac{e \cdot E \cdot a}{2 \cdot k_B \cdot T}\right] \quad (1)$$

which contains terms accounting for both thermally activated conductivity and for electric field enhanced conductivity. Separation of these terms allows each behavior to be tested independently.

While it is relatively easy to determine carrier density and mobility in semi-conductors, the same quantification is complicated in insulating polymers. Concentrations of impurity atoms or chains are difficult to quantify, the polymer chains do not lend themselves to the simplifications of a lattice construct, and polar groups attached to the chains have significant influence on carrier mobility. These polar groups can also contribute to an overall material polarization that influences the internal electric field felt by the carriers [5]. In reality, material thickness introduces the complexity of multiple layers of trapping sites. Accurate determination of the trap depth and distribution is extremely difficult. To address this complexity, it is assumed that shallow traps provide the bulk conductivity while deep traps are not considered to be involved in carrier mobility [4,5].

Despite the differences in morphology, many polymers show remarkably similar behavior to more ordered materials. Specifically, the conductivity shows electric field dependence. Application of an electric field across the sample lowers the activation energy needed for the electron to hop the potential barrier [3,4].

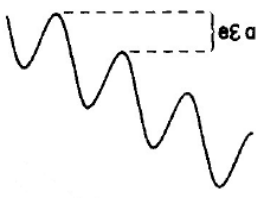

Fig. 2 Application of an electric field enhances the hopping conductivity by lowering the amount of energy need to move between trap sites.

For constant temperature conditions, the enhanced conductivity due to the applied field follows Poole-Frenkel behavior [6] such that

$$\rho(E;T) = \rho_0(T)\exp\left[-\frac{\beta\ E^{0.5}}{k_B \cdot T}\right] \qquad (2)$$

where β is the Poole-Frenkel coefficient and is dependent on the charge of the carrier and the dielectric constant of the material [7,8],

$$\beta = \left(\frac{e^3}{\pi\cdot\varepsilon\cdot\varepsilon_0}\right)^{\frac{1}{2}} \qquad (3)$$

For LDPE and assuming electrons as the charge carriers, the calculated value is approximately 5.05 x 10^{-5} eV $m^{1/2}$ $V^{-1/2}$ for a dielectric constant ε = 2.26.

Verification of Poole-Frenkel behavior in the literature is limited largely to the high field limit [5]. This stems from the origin of the model, in which the hopping conductivity becomes independent of the electric field in the low field limit. Very low applied electric fields are the region of interest for the following experimental work.

Experiment

Resistivity of an insulator can be found using the thin film capacitor approximation [9,10]. For highly resistive materials, this involves measurements of extremely small currents and the presence of a polarization field within the material can influence the relevant time scale of the measurements. The most common method is the constant voltage method [11]. A thin film sample is placed between two metal electrodes, a voltage is applied across the sample, and the leakage current is measured.

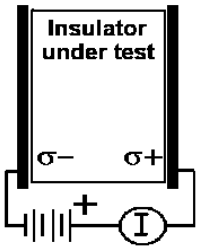

Fig. 3 – Diagram of constant voltage method as an approximation of a thin film capacitor.

The sample material chosen was low density polyethylene, a widely used and well-characterized semi-crystalline polymer. LDPE samples of two thicknesses, 125 mil and 5 mil, were chemically cleaned with methanol and placed in a constant voltage apparatus in a vacuum chamber at a pressure of 10^{-4} torr. Applied voltages ranged from approximately 0.16% to 1.4% of the breakdown voltage as given by the material manufacturer [7,8]. All samples were maintained at a constant voltage and temperature for one hour and the long-term current limit was used to calculate the resistivity in order to eliminate contribution by the short-term polarization current that develops under an applied field [5]. Calculated resistivity for both thicknesses as a function of the percentage of breakdown voltage is shown in Fig. 4.

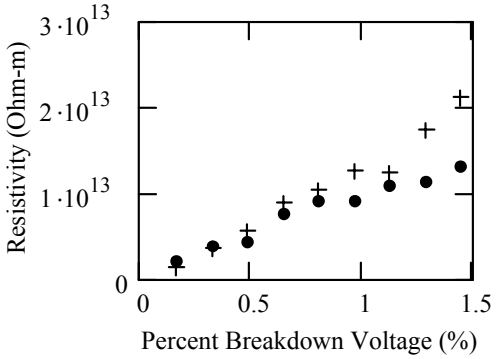

Fig. 4 Calculated resistivity as a function of percentage of breakdown voltage. Resistivities for the 125 mil and 5 mil samples are solid circles and plus signs respectively.

The resistivities of the two samples show good agreement at less than 0.5% of breakdown voltage but diverge quickly, with the 5 mil sample resistivity showing greater dependence on the applied electric field than the 125 mil sample.

For LDPE to follow Poole-Frenkel behavior, a linear relationship between the log of the conductivity and the square root of the electric field is expected. Applying a simple linear regression finds that both the 125 mil and the 5 mil show Poole-Frenkel behavior, as seen in Fig.5.

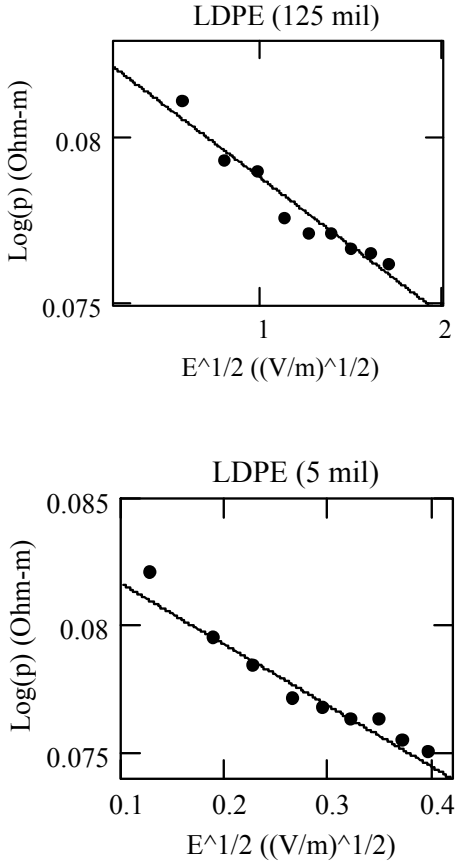

Fig. 5 Linear regression fits for LDPE samples. Correlation coefficients for the 125 mil and 5 mil samples were 0.970 and 0.974 respectively, indicating a strong correlation between the resistivity and the applied electric field.

Conclusions

Confirmation of Poole-Frenkel would be a significant step toward verifying that hopping conductivity and field-enhanced conductivity are valid mechanisms for charge transport in LDPE.

From the linear regression fits using the calculated resistivities strongly indicate that LDPE follows Poole-Frenkel behavior at low applied fields as well as high applied fields. However, the experimental value of the Poole-Frenkel coefficient calculated for the 125 mil sample is 3.60×10^{-7} $eVm^{1/2}V^{-1/2}$ and for the 5 mil sample the experimental value of β is 2.11×10^{-6} $eVm^{1/2}V^{-1/2}$. The experimental values for the samples differs by one or two orders of magnitude, suggesting that while the data appears to exhibit Poole-Frenkel behavior, more investigation of LDPE is necessary.

References

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