1-1-2007

Dependence of Resistivity in Low-Density Polyethylene on Space Environment Parameters

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Recommended Citation

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Abstract

The conductivity of high-resistivity polymer films is dependent on the magnitude of applied electric field, repeated electric field exposure, and sample temperature. A traditional constant voltage method was used, maintained under vacuum to more closely resemble the space environment. Both the strength of the applied voltage and the thickness of low-density polyethylene (LDPE) samples were varied to determine the electric field dependence of internal polarization and the leakage current most appropriate in calculating the resistivity. Repetition of same field strength measurements determined the influence of sample history and charging memory. Measuring the resistivity from cryogenic temperatures to well above the glass transition temperature of LDPE allowed for separation of hopping conductivity regimes and correlation with internal morphology. In combination, these measurements provide a picture of the resistivity behavior of LDPE.

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].

Modeling and understanding the complex relationships between the spacecraft and its surroundings is fundamentally based on a detailed knowledge of how individual materials store and transport charge. The low charge mobility of insulators causes charge to accumulate where deposited, preventing even redistribution of charge and creating differing local electric fields and potentials. Effects of local potential differences can range from any number of systematic errors, arcing to external plasmas, and in the extreme case, complete system failure due to a charge pulse generated by breakdown of the insulating material [1]. Long-term accumulation of charge can cause degradation of exterior surfaces of the spacecraft, enhance contamination of the materials, and cause inaccuracies in the analysis of the properties of the space environment. The history of the sample becomes important as the behavior of the material is modified with further charging [2,?]. Increasing the versatility and reliability of spacecraft charging models and expanding the database of information for the electronic properties of insulating materials can assist spacecraft designers to accommodate and mitigate these harmful effects [3]. Improving the design models requires a better understanding of the physics of materials, particularly with respect to insulating polymers. The resistivity of the material is a key transport parameter in determining how deposited charge will distribute across the spacecraft, how rapidly charge imbalances will dissipate, and what equilibrium potential will be established under given environmental conditions [4]. Charge is deposited on the spacecraft surfaces as it orbits, making the orbital or rotational periodicity the relevant time scale.

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Hence, it is critical for reliable spacecraft charging models to have appropriate values of resistivity for typical thin film insulators in order to determine the correct charge storage decay times for the materials. The bulk resistivity values of commonly used insulators have most often been found using classical ASTM prescribed methods [5], such as the constant voltage method. These standard methods are limited in their range of measurable resistivities and are not strictly applicable to common situations encountered in spacecraft charging [6,7]. But instrumentation is only the first challenge.

The 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 conductivity of the material, and its inverse, the resistivity $\rho = 1/\sigma$, is the relevant property for determining mobility of charge carriers and dissipation rate of accumulated charge within the material; and the most promising theoretical possibilities for explaining electrical behavior in insulating polymers are concepts and hopping conductivity models that have proven successful in application to semi-conductors and amorphous solids [3,4]. These theories are well tested for semi-conductors, but remain largely unverified for insulators [5].

Fundamental assumptions of the successful hopping 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 well depth or traped site binding energy and well separation, respectively [4,5].

The electron, or hole, moves through the material by hopping between 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].

In reality, the finite thickness of the sample introduces multiple layers of trapping sites and can significantly change the density of charge carriers, n(T). It is assumed, for simplicity, that shallow traps provide the bulk conductivity while deep traps do not contribute to charge mobility [4,5].

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]. An example of transient polarization currents in LDPE is shown in Fig. 2.
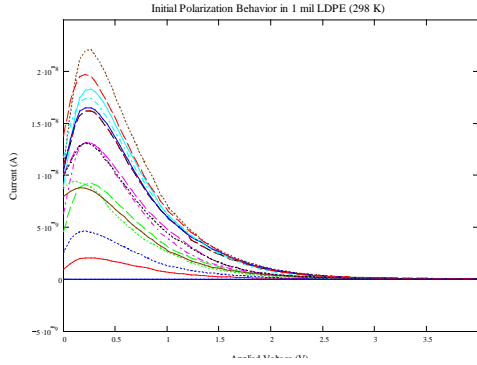
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Fig. 2. Initial current due to internal polarization and response of 1 μm LDPE to an applied electric field. Applied voltages (V) :30, 70, 140, 200, 280, 340, 410, 480, 550, 620, 690, 760, 830, 900, and 1000 V.

Initial polarization currents, the strength and behavior of which vary from material to material, must be allowed to decay before the leakage current through the material can be measured. For the constant voltage method, a macroscopic first-principles model has been developed [] that contains both the initial current due to polarization and the long-time leakage current though the material.

$$I_{CV}(t) = I_P(t) + I_{Leak} = V_{CV}\, C_o \left[\left(\frac{\varepsilon_r^\infty - \varepsilon_r^o}{\tau_P} \right) e^{-t/\tau_P} + \frac{\varepsilon_r^\infty}{\tau_{DC}} \right]$$

(1)

Other relevant terms in Equation 1 are the relative dielectric constant of the material, ε_r, free air capacitance, C_o, and the decay times of internal charge, τ_{DC}, and material polarization, τ_P. This model can be used to approximate the length of time needed for the polarization current to decay. In the case of LDPE, a measurement time of one hour is sufficient to ensure that all polarization currents have ceased to contribute to the leakage current.

The resistivity is dependent on carrier mobility, which in turn is influenced by both temperature, T, and applied electric field, E. In general, the probability of hopping is directly related to resistivity such that,

$$\rho_{hop}(E,T) = \left[\frac{2 \cdot n(T) \cdot v \cdot a \cdot e}{E} \right]^{-1} \exp\left[\frac{\Delta H}{k_B \cdot T} \right] \cosh\left[\frac{\varepsilon \cdot E \cdot a}{2 \cdot k_B \cdot T} \right]$$

(2)

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. Other parameters that appear in Equation 2 are the frequency of hops, v, the dielectric constant, ε, the density of charge carriers, $n(T)$, the well depth, ΔH, and well separation, a.

Application of an electric field across the sample lowers the activation energy needed for the electron to hop the potential barrier [3,4].
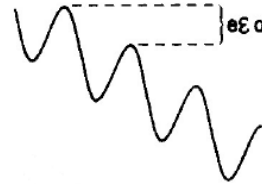

Fig. 3. Application of an electric field enhances the hopping conductivity by lowering the amount of energy need to move between trap sites.

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

$$\rho(E;T) = \rho_o(T) \exp\left[-\frac{\beta\, E^{0.5}}{k_B \cdot T} \right] \qquad (5)$$

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],

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

Using Equation 3 for LDPE and assuming electrons as the charge carriers, the calculated value is approximately 5×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ for a dielectric constant $\varepsilon = 2.26$. This equation, while successful in the field of amorphous semiconductors, has not been verified for polymers.

Investigation of the 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. The first purpose of this experimental work was to test the electric field dependence of LDPE and determine if it shows Poole-Frenkel behavior in the limit of high applied electric fields. Observation of this behavior would suggest that hopping conductivity is a viable model for LDPE.

The second purpose of this work was to determine the temperature dependence of resistivity. This relationship is vital because hopping conductivity is fundamentally a phonon-assisted mechanism [12]. The charge carriers are unable to transition between localized, bound states without phonon interaction. This leads to inherent temperature dependence in the probability of hopping and in the measured current due to hopping charge carriers. The temperature dependence of resistivity in LDPE was determined as follows.

Low-density polyethylene is a good candidate for attempts to verify hopping conductivity models. It is one the most common and versatile polymers; high uniformity and high purity samples can easily be obtained for testing. Much is known about LDPE and it is relatively well characterized. LDPE is also semi-crystalline, which increases the likelihood that hopping conductivity is an appropriate model for LDPE. The relatively low estimated resistivity of LDPE, on the order of 10^{17} Ohm-cm, means that it is measurable using the constant voltage method, which is the most common method as well as the easiest method to achieve in the laboratory.

Experiment

Resistivity of an insulator can be found using the thin film capacitor approximation [9,10]. 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. For highly resistive materials, this involves measurements of extremely small currents and the presence of a polarization field within the material influences the relevant time scale of the measurements.
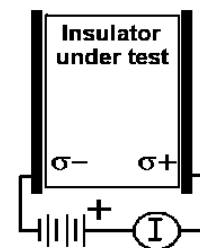

Fig. 4. Diagram of constant voltage method as an approximation of a thin film capacitor.

Two 25 μm LDPE samples of identical origin were chemically cleaned with methanol and baked at 65($\pm$1)$^{\circ}$C

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under vacuum of approximately 10^{-5} torr for two days to eliminate water that may have been absorbed during processing and handling. The samples were placed in a constant voltage apparatus inside a vacuum chamber maintained at a pressure on the order of 10^{-5} torr.

Two samples were used in this experiment rather than one because it has been shown in previous work [13] that charging history and repeated applied voltages have an effect on the resistivity of the sample. The samples were obtained from the same manufacturer and were cut from the same allotment of material, ensuring as near to identical composition, properties, and environmental history as possible.
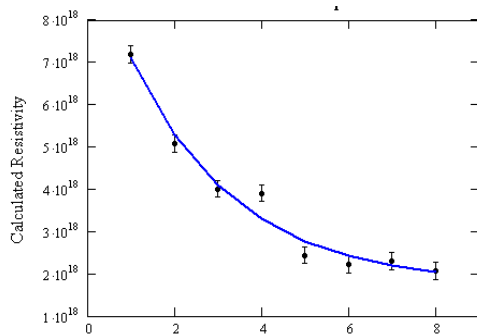

Fig. 5. Repeated measurements of resistivity of LDPE under the same applied voltage.

To determine electric field dependence, the sample was placed under an applied voltage for one hour and then allowed a thirty minute recovery period with no applied voltage before the next applied voltage. A summary of applied voltages is shown in Table 1. The sample suffered dielectric breakdown at 1100 V, allowing for the percentages of breakdown to be accurately calculated.

For each experimental run, the average of the measured leakage current at the end of the hour was calculated and plotted as a function of applied electric field.

Applied Voltage (V)	Percent Breakdown
30	3%
70	6%
140	13%
200	18%
280	26%
340	31%
410	37%
480	44%
550	50%
620	56%
690	63%
760	69%
830	76%
900	82%
1000	91%

Table 1. Applied voltages and associated percentage of breakdown for 25 μm LDPE at 298 K.

A linear regression was used to fit the current and applied electric field data, with an R-squared value of 0.99. The results are shown in Fig. 6.
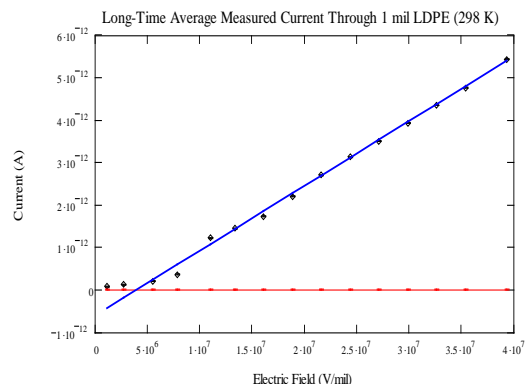

Fig. 6. Average long-time leakage current through 25 μm LDPE at 298 K with linear regression fit.

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Since resistivity is the relevant quantity in determining whether or not hopping conductivity is a viable model for LDPE, the average long-time current was used to calculate the resistivity at each applied voltage. The log of the resistivity was then plotted as a function of $E^{1/2}$, see Fig. 7.
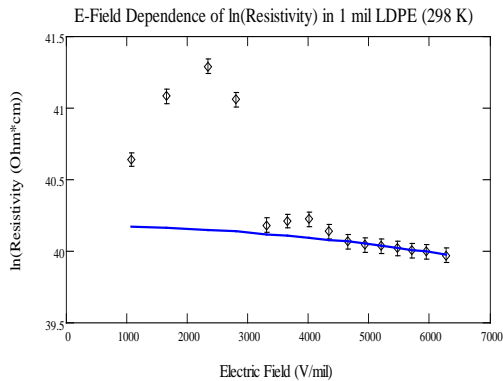

Fig. 7. Ln calculated resistivity as a function of $E^{1/2}$ with linear fit to data corresponding to 50% to 90% of breakdown voltage.

Below 280($\pm$1) V, no good mathematical fit could be found to adequately fit the data and it was determined that the resistivity was independent of applied electric field below 18% of breakdown voltage. Above 550($\pm$1) V, corresponding to 50% of breakdown, the applied field dependence indicates Poole-Frenkel behavior and the linear regression fit of ln ρ and $E^{1/2}$ has an R-squared value of 0.99. Between 280($\pm$1) V and 550($\pm$1) V, linear regression produced only a moderate fit, suggesting an intermediary dependence on applied electric field. Determining β, the Poole-Frenkel coefficient, gives 5×10^{-6} eV m$^{1/2}$ V$^{-1/}$. This is an order of magnitude smaller than the theoretical calculation of β using Eq.3 and serves as a reminder of the fundamentally more complicated charge transport behavior even in a simple polymer.

Investigation of the temperature dependence of resistivity of LDPE included two stages. First, the sample not previous used was placed under an applied voltage of 140($\pm$1) V, which corresponds to approximately 10% of breakdown voltage, the leakage current was measured for an hour at room temperature, 23($\pm$2)$^{\circ}$C, (see Fig.8). The resistivity was then calculated using the long-time, steady state limit and found to be 8.17($\pm$0.08) x 10^{17} Ω-cm. Note the influence of the initial polarization current clearly visible in Fig. 8.
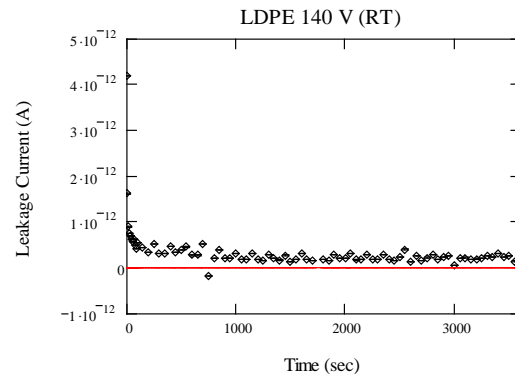

Fig. 8. Leakage current through 25 μm LDPE sample at 140($\pm$1) V at 23($\pm$2)$^{\circ}$C for one hour. The straight red line below the data points is the base noise level of the system while all equipment is powered on but no measurements are being taken.

The chamber and sample were then cooled to -40.0($\pm$0.5)$^{\circ}$C using liquid nitrogen and, once equilibrium was reached, placed under an applied voltage of 140($\pm$1) V. The lower bound of the experimental temperature range was chosen to avoid possible onset of ill-defined behavior due to approaching the glass transition temperature, which ranges from -60°C to -125°C in the literature, depending on the reporting source and manufacturer. Measured leakage current through such a phase transition would be unlikely to be due to hopping conductivity alone and is

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therefore be beyond the scope of this research.

Once temperature equilibrium was reached, the chamber and samples were then allowed to return to room temperature without the aid of internal or external heating and the leakage current was monitored throughout the warming period. A typical warming period without intervening heating lasts approximately twenty hours, corresponding to an average warming rate of approximately 3°C per hour. After the sample had returned to room temperature, a second heating apparatus was connect to the chamber and the sample temperature was raised to 55($\pm$0.5)^{o}C. The upper bound of the experimental temperature range was chosen to remain well within the working temperature range given by the manufacturer []. The samples was then placed under an applied voltage of 140($\pm$1) V and allowed to cool without external or internal aid, corresponding to a rate of approximately -2°C. The measured leakage current over the course of the entire temperature range is shown in Fig. 9
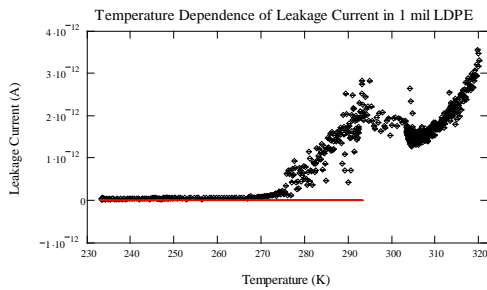

Fig. 9. Leakage current through 25 μm LDPE sample from -40.0($\pm$0.5)^{o}C to 55($\pm$0.5)^{o}C. The straight red line below the data points is the base noise level of the system while all equipment is powered on but no measurements are being taken

At low temperatures, the current approaches the instrumentation limit of the Keithley 616 picoammeter and the leakage current is barely distinguishable from the base noise level of the system. The base noise level alone corresponds to a resistivity of 6($\pm$ 1) x 10^{19} Ω-cm. The current increases slowly until the temperature reaches approximately -5($\pm$0.5)^{o}C where it rises suddenly, corresponding to an order of magnitude drop in resistivity as T increases to room temperature. During the heating stage, the current remains relatively stable before rising significantly once the temperature passes approximately 34($\pm$0.5) ^{o}C.

Comparing the calculated resistivity at regular intervals throughout the temperature range with the calculated resistivity at room temperature reveals that the resistivity is indeed dependent on temperature, as seen in Fig. 10.
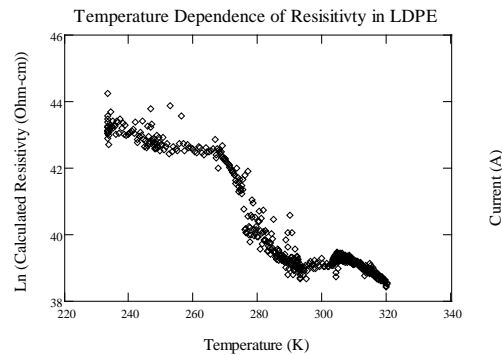

Fig. 10. Calculated resistivity as a function of temperature in 25 μm LDPE from -40.0($\pm$0.5)^{o}C to 55($\pm$0.5)^{o}C.

In the low temperature range, the resistivity is significantly increased. This behavior theoretically corresponds to lower carrier mobility and a decrease in hopping conductivity probability. However, it was discovered during the experimental process that the leakage current was strongly effected by heating or cooling rates. More work and instrumentation will be required to

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ensure that a changing rate is not a significant factor in the temperature dependent behavior of the resistivity.

Data Analysis

To confirm hopping conductivity as an appropriate model for charge transport in LDPE, the resistivity must be inversely proportional to temperature in a range where it is energetically favorable for an electron to hop to nearest neighbor states. The temperature dependence must transition to a $T^{-1/4}$ in the low temperature limit, corresponding to the theoretical onset of variable-range hopping where it is energetically favorable for the electron to hop to lower energy states beyond the nearest neighbor states [14]. Using Eq. 2, the resistivity at should be proportional to an exponential with powers of T^{-1} and $T^{-1/4,}$ according to the temperature range.

Plotting the log of the calculated resistivity as a function of temperature, three regions with distinct behavior are observed.
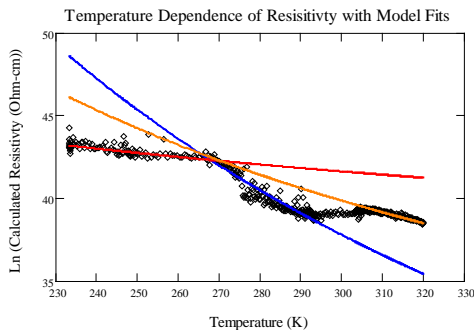

Fig. 11. Temperature dependence of the log of calculated resistivity in 25 μm LDPE with linear regression fits corresponding to regions of $T^{-1/4}$ (shown in red) and 1/T (shown in blue and orange) dependence. Temperatures are in Kelvin.

Below -(±0.5)^{o}C, the resistivity follows the $T^{-1/4}$ dependence expected for variable range hopping (shown in red in Fig. 8). Between -5(±0.5)^{o}C and 19(±0.5)^{o}C, the resistivity is inversely proportional to T, (shown in blue in Fig. 8). There is a plateau in resistivity between 19(±0.5)^{o}C and 39(±0.5)^{o}C that may or may not be due to the slower heating rates as the sample and chamber approach room temperature. Above 39(±0.5)^{o}C, the behavior is again inversely proportional to T (shown in orange in Fig.11).

The point at which the low temperature behavior transitions must correspond to a physical, morphological phase transition within the material, but it is unknown what that transition is.

Conclusions

At constant temperature, the resistivity of LDPE is independent of applied electric field below field strengths of 18% of breakdown. Above 50% of breakdown, the resistivity follows Poole-Frenkel behavior. Calculation of the Poole-Frenkel coefficient, β, from Eq. 3 is an order of magnitude different from determination of β using the fit of the data. This discrepancy is not unexpected due to the complex nature of the material; the applicability and appropriate form of Eq. 3 has not been determined for polymers. Between 18% and 50% of breakdown, the resistivity shows a weak dependence on applied electric field.

The resistivity of LDPE shows two regimes of temperature dependence. At low range temperatures, a $T^{-1/4}$ dependence is observed that could suggest variable range hopping as a mechanism. At higher temperatures, the resistivity is inversely proportional to temperature; behavior that is also consistent with hopping conductivity as

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a model of phonon-assisted charge transport. However, more research is needed to eliminate mechanisms that behave similarly and result in similar temperature dependence. It is also necessary to develop an adequate method of maintaining uniform heating rates to ensure that the temperature dependence of resistivity is truly being measured.

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