Time-Evolved Constant Voltage Conductivity Polymeric Materials

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Abstract—Long-duration conductivity measurements were made for low density polyethylene (LDPE), polyimide (PI), polyether ether ketone (PEEK), and biaxially-oriented polypropylene (BOPP) to determine their bulk conductivity near room temperature as a function of time. These common thin-film spacecraft material samples were vacuum baked to remove moisture and volatile contaminants to better simulate space conditions. The constant voltage conductivity (CVC) method used a very stable, low-noise DC voltage source and measured the resulting current in a parallel plate geometry. Due to the extremely low conductivity of these four polymeric materials, extended experiments of up to 10 days were necessary to establish equilibrium current flow and determine dark conductivity. The lower instrumental limit of conductivity measurements with this setup is \( \lesssim 2 \times 10^{-21} \, \text{(Ωcm)}^{-1} \). Changes in conductivity due to field-enhanced conductivity and radiation induced conductivity as well as varying voltages, temperatures and dose rates are also considered.

Data for each material are fit to a multi-term model to account for the different conduction mechanisms within highly disordered insulating materials (HDIM), including polarization, dispersive transport, and dark conductivity. The regimes of disorder-induced dispersive transport demarcated by the transit time are observed in all materials, indicative of hopping transport between trap states in HDIM. Information on the energy distribution of localized trap states responsible for electron conduction in HDIM is extracted from the fitting parameters. Magnitudes and time-dependence of conductivity are reported, along with estimated polarization, transit, equilibrium, and decay times; these are compared favorably with previous measurements using constant voltage and charge storage decay conductivity methods. These fits can be used with model simulations of time-dependent spacecraft charging to determine non-equilibrium transient conductivity for specific applications.

Index Terms—Conductivity, Constant Voltage Conductivity, Disordered Materials, Electron Transport, Polymers, Resistivity, Temperature Assisted Hopping, Variable Range Hopping.

I. INTRODUCTION

Charging effects on spacecraft have been extensively documented and researched in an attempt to prevent critical failure of key spacecraft components [1,2]. Charge exchange between the craft and its radiation environment and charge transport within spacecraft materials pose a complex problem on both macroscopic [1] and microscopic [3,4] scales. These traits of charge accumulation, dissipation and transport are characterized by material properties including conductivity, radiation induced conductivity, permittivity, electrostatic breakdown, electron emission, and cathodoluminescence [2].

Thin film and bulk polymeric highly disordered insulating materials (HDIM), such as the four materials studied here, are ubiquitous in spacecraft. These materials inhibit charge transport very well, and therefore can appreciably store charge due to their long decay time and create charge imbalances that can lead to deleterious electrostatic discharge (ESD) events [1,2,5]. Determining accurate values for conductivity, particularly equilibrium dark current conductivity (\( \sigma_{DC} \)), of these materials is essential to calculate and model internal charge storage and movement on spacecraft [6,7]. However, the same extremely slow transport and long equilibration times that enhances charge accumulation making the study of these materials critical, also makes their measurements a challenge [4,8,9]. The extreme disorder of HDIM also makes their underlying materials physics both unique and complex [3]. Thus, understanding the temporal evolution of measurements under applied field and the underlying transport mechanisms of HDIM due to the extreme insulating properties and highly disordered structure of these materials, has proven difficult.

The focus of this study is the time evolution of conductivity as measured with the Constant Voltage Conductivity (CVC) test method. This study builds on previous work focused on the measurement, experimental uncertainties, modeling and underlying physics after samples have come to equilibrium in these measurements [8,9]. Section II provides a brief review of relevant transport theory for HDIM. A model for the time-dependent conductivity incorporating polarization, dispersive transport, and equilibrium conductivity is introduced, and the relative importance of the different conduction mechanisms on different times scales is discussed. Sections III and IV present experimental details and discuss experimental and systematic uncertainties, including those due to non-equilibrium voltages, temperatures and dose rates. Section V reports long-duration measurements and comparison of the magnitudes and time-

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dependence of conductivity for four polymeric materials with the model.

II. THEORY

Understanding the electrical conduction of very good insulators—both very wide bandgap insulators and HDIM—cannot be directly understood in terms of familiar band structure concepts used for crystalline semiconductor materials. Through the quantum mechanical treatment of the long-range order of crystalline semiconductors, conduction by promotion of charge carriers across well-defined band gaps has come to be the welcomed conceptual norm for explaining electron transport.

However, the distinction between extended states resulting from long-range order, and spatially localized trap states resulting from disorder found at energies within the bandgap is a defining feature of charge transport in amorphous solids and HDIM. For HDIM, the density of states (DOS) of such disordered localized states has its energy distribution characterized by a width parameter $\alpha$ [3,4,10]. Conduction is described in terms of discrete transitions between spatially localized states through tunneling hopping mechanisms, such as thermally-assisted hopping and nearest-neighbor (or variable-range) hopping [4,10]. One can characterize conduction in terms of the time it takes charge to traverse a material via hopping. For transport involving only a single trap state energy (i.e. $\alpha \to 0$), charge motion in a parallel plate geometry is a diffusive process with time dependence of the form $t^{-1\alpha}$. Conduction is characterized by a transit time $\tau_{\text{trans}}$, the time for a charge front to move across a sample [3]. In HDIM there is a distribution of times for charge carriers to move from one trap to the next and across the sample, as carriers have longer retention times in more tightly bound trap states. Therefore, the injected internal charge distribution expands across an HDIM sample, with the majority of the charge density staying near its origin. There is a displacement current contribution to measured current as the charge distribution is modified, even before charge has moved across the full width of the sample.

This leads to conductivity behavior unique to HDIM that results from hopping between localized defect trap states with a distribution of energies. This was first explained by Scher and Montroll [11] for charge transport across disordered semiconductors, and later extended to HDIM, as

$$I(t) = \begin{cases} I_0 t^{-(1-\alpha)} \theta(\tau_{\text{trans}} - t), & \text{for } t < \tau_{\text{trans}} \\ I_0 t^{-(1+\alpha)} \theta(t - \tau_{\text{trans}}), & \text{for } t > \tau_{\text{trans}} \end{cases} \quad (1)$$

The first term, dispersive transport, models times before the leading edge of the charge front reaches the rear electrode at $\tau_{\text{trans}}$, and the second term describes transitive transport for times after $\tau_{\text{trans}}$. The Heaviside function, $\theta(t)$, is used to separate these terms temporally. $\alpha$ is a parameter that describes the distribution width of the localized DOS, where $0 \leq \alpha \leq 1$ [3]. Weak disorder leads to narrow distributions of defect state energies, and dispersive and transitive transport merge to diffusive transport in the limit $\alpha \to 0$. $\alpha$ is an intrinsic property of a material and can only be changed by modifying the distribution of states, for example by chemical modifications, mechanical deformation, or a total incident radiation dose.

Charge transport in the parallel plate configuration is modeled macroscopically from Ohm’s law in terms of the conductivity as

$$\sigma(t) = \frac{\mathcal{J}(t)/\mathcal{E}(t)}{[l(t) \cdot d]/[V(t) \cdot A]}, \quad (2)$$

where $I(t)$ and $V(t)$ are the measured time-dependent current and applied voltage, and $d$ and $A$ are the time-independent sample thickness and electrode area, respectively.

The total conductivity has been previously modeled for a variety of applications with time-dependent macroscopic models for a number of conduction mechanisms that includes polarization, dispersive transport, dark current conductivity, radiation induced conductivity, AC conductivity, and displacement currents resulting from time-dependent changes in applied voltage and permittivity (see more detailed treatment in Appendix B of ref. [8]). For the CVC method it is shown that the conductivity can be expressed as [8]

$$\sigma(t) = \sigma^0_\text{d} e^{-\tau_{\text{trans}}/(1-\alpha)} \theta(\tau_{\text{trans}} - t) + \sigma^0_\text{p} e^{-(1+\alpha)\tau_{\text{trans}}} \theta(t - \tau_{\text{trans}}) + \sigma_\text{DC}. \quad (3)$$

The initial term in Eq. (3) is a polarization displacement current, which results from the response of the internal charge of the material to the applied electric field, essentially a time-dependent permittivity $\varepsilon(t)$. For many materials, this exponential decay dominates the conductivity for short time periods, until the material has mostly responded to the applied field. This idealized relaxation model is characterized by a polarization time constant, $\tau_p$. Relatively short time constants for electronic, atomic, molecular and interfacial responses can range from the very fast—well below time scales measured in typical CVC tests—to perhaps $10^2 \text{ s}$ to $10^3 \text{ s}$. Measurements will often exhibit more than one time constant and amplitude associated with different response mechanisms.

For longer time scales, the conductivity is dominated by the dispersive displacement current, i.e. the components of Eq. (1) discussed above. Both terms fall off as power laws of time; the dispersive term at shorter time with a smaller time constant $(1-\alpha)$, and the transit term at longer time with a larger time constant $(1+\alpha)$. The signature of the transition at $\tau_{\text{trans}}$ is most evident in a log-log plot of current versus time, where both terms are linear and there is a distinct change in slope at $\tau_{\text{trans}}$, as the transport mechanism shifts from the dispersive to the transitive regime. If the Scher and Montroll model is applicable, the fitting parameter $\alpha$ is the same for the dispersive and transitive terms, that is the sum of the slopes before and after $\tau_{\text{trans}}$ is $[(1-\alpha) + (1+\alpha)]=2$. For disordered semiconductors $\tau_{\text{trans}}$ is in the range of $10^{-6} \text{ s}$ to $10^{-1} \text{ s}$ [3,11], while for HDIM $\tau_{\text{trans}}$ can range from $10^3 \text{ s}$ to $10^5 \text{ s}$ as trap state energies and disorder increase.

The final term, $\sigma_\text{DC}$ or dark conductivity, is the equilibrium time-independent conductivity of electron transport across the material reached after long time spans as the charge distribution within the material becomes uniform and the change in the dispersive displacement current become negligible. One time scale related to $\sigma_\text{DC}$ is the time to equilibrium, $\tau_{\text{eq}}$; this can be difficult to accurately identify if the dark current is very small.
or there are other contributions—discussed in Sec. IV—that cause changes in the dark current. From an operational point of view, \( \tau_{eq} \) is defined here as when the contribution from the transitive current becomes smaller than the noise in the dark current, \( \sigma_{trans}(\tau_{eq}) = \Delta \sigma_{DC} \).

Another related time scale is the decay time, \( \tau_{decay} \equiv (\varepsilon_0\varepsilon_r/\sigma_{DC}) \), for a charge layer deposited on a surface to discharge to \( 1/e \) of the initial charge; it is simply the intrinsic form of the RC time constant of a discharging capacitor and is what is measured in charge storage (or surface voltage decay) conductivity (CSC) experiments to determine \( \sigma_{DC} \). One could expect that \( \tau_{eq} < \tau_{decay} \), since the electric field driving charge is maintained for CSC experiments while the electric field diminishes as charge is dissipated in CSC measurements. For a relative permittivity of \( \varepsilon_r=3 \) (typical for polymers), \( \tau_{decay} \) varies from \( 10^4 \) s (3 hr) to \( 10^8 \) s (4 yr) for conductivities of \(~3\times10^{-17} \text{(} \Omega \cdot \text{cm})^{-1} \) to \(~2\times10^{-21} \text{(} \Omega \cdot \text{cm})^{-1} \), respectively.

The various time scales outlined above can be arranged in an expected order of increasing times as

\[
\tau_Q < \tau_p < \tau_{transit} < \tau_{eq} < \tau_{exp} < \tau_{decay} .
\]  

The time scales related to the conduction mechanisms—\( \tau_p \), \( \tau_{transit} \), \( \tau_{decay} \), and \( \tau_{eq} \), are bracketed here with two experimental time scales. \( \tau_{exp} \) is simply the duration of the CVC measurements, which in an ideal experiment, always exceeds the time to equilibrium \( \tau_{eq} \). \( \tau_p \) is the time to establish the initial charge (voltage) on the electrodes; this includes contributions from the voltage supply response time and the charge injection process [8]. Typically, \( \tau_Q \lesssim 0.2 \) s (\( \tau_Q \lesssim 10^{-2} \) s for the battery voltage supply used here) and is therefore not evident in the data shown here.

### III. Experimental Setup

A schematic of the Constant Voltage Conductivity (CVC) test apparatus [8] is shown in Fig. 1, illustrating the electrical and computer interface connections and the configuration with samples sandwiched between two parallel plate electrodes. Sample current, applied voltage, and temperature data are recorded by a custom \textit{LabView} \textsuperscript{TM} program through a computer interface. Currents and voltages are recorded at \(~3\) s intervals, except during the initial minutes of each experiment where \( \leq 1 \) s interval can be used. Temperature is recorded at \(~10\) s intervals.

An aluminum plate serves as the front high-voltage electrode on which samples are mounted. A highly-polished (1.98±0.02 cm\(^2\)) copper guarded rear electrode held near ground is used to monitor the sample current. The test fixture clamps the electrodes to the sample with calibrated springs that provide \(~300 \) kPa pressure, in compliance with the ASTM D257 standard [12]. This entire assembly is housed in a high vacuum chamber at vacuum, experimental runs commenced. Background currents with grounded samples were recorded for prolonged periods at the beginning and end of each run, so that linear drift in any small instrumentation offset current could be subtracted from the measured data. Runs lasted until the samples reached current equilibrium, which took up to tens of days. Once equilibrium was reached, the voltage source was shut off and the discharge current versus time was recorded. Using measured values for the time-independent sample thicknesses and electrode area, the time-dependent conductivity was then determined with Eq. (3) and modeled with Eq. (4).

Well-characterized, high-uniformity polymer samples from Goodfellow were used for all tests.

- Low density polyethylene (LDPE) samples (ASTM D-5213 type I [14]) tested had measured thicknesses of 27.4 \( \mu \text{m} \pm 0.7\% \), density of 0.92±0.01 g/cm\(^3\) [15], estimated...
crystallinity of 50% [16], a peak fractional mass
distribution of ~6·10^3 amu [9, 18], and $e_v=2.27±0.08$ [15].
Measurements were made at 420 V, or ~17 MV/m.
- Polyimide (PI) samples of Kapton HN (ASTM D-5213
type I [14]) had measured thicknesses of 25.0 μm ±2%,
density of 1.43±0.01 g/cm^3 [19], and $e_v=3.5±0.1$ [19].
Measurements were made at 800 V, or ~32 MV/m.
- PEEK samples had measured thicknesses of 29.6 μm ±1%,
density of 1.26±0.005 g/cm^3, and $e_v=3.25±0.05$ [20].
Measurements were made at 800 V, or ~32 MV/m.
- BOPP samples tested had measured thicknesses of 27.6 μm ±1%,
density of 0.90±0.05 g/cm^3 [21], and $e_v=2.4±0.2$ [21].
Measurements were made at 800 V, or ~32 MV/m.

All samples were chemically cleaned with methanol prior to
a bake out at ~385±5 K (338±3 K for LDPE, as the melting
point for LDPE lies around 383 K) under <10^-3 Pa vacuum for
≥4 days while in contact with a grounded surface, to eliminate
absorbed water and volatile contaminants and any residual
stored charge [9]. After bake out, samples were mounted on
voltage plates and stored in a dry nitrogen environment until
ready for measurements.

Nominal dark current conductivity for unbaked samples
using standard ASTM 257 test methods [12] and breakdown
field strengths for unbaked samples using standard ASTM 149
test methods [24] were listed as ~8·10^{-17} (Ω·cm)^{-1} and 200
MV/m for LDPE [16], ~1·10^{-18} (Ω·cm)^{-1} and 303 MV/m
for PI [19], ~2·10^{-16} (Ω·cm)^{-1} and 200 MV/m for PEEK
[20], and ~1·10^{-17} (Ω·cm)^{-1}, and 110-150 MV/m for BOPP
[21], respectively. The nominal breakdown voltages as
determined by a 2-parameter Weibull fit for vacuum baked
samples were measured as 316 MV/m for LDPE, 272 MV/m
for PI, 200 MV/m for PEEK, and 337 MV/m for BOPP,
respectively [22].

IV. EXPERIMENTAL UNCERTAINTIES

Instrumental limits on the precision and accuracy of
measured conductivity associated with the four measured
quantities in Eq. (3) are set by a number of factors. Uncertainty
in lower conductivities is dominated by the precision in the
current measurements of ~1 fA [8]. This corresponds to a
resolution limit of measured conductivity of $\Delta \sigma_{res} = 2·10^{-24}
(\Omega\cdot cm)^{-3}$ for typical values of $V$, $d$ and $A$. When samples reach
equilibrium currents, signal averaging of measurements over
10^3 s can typically reduce the precision to ~1·10^{-16} A and
$\Delta \sigma_{res} = 2·10^{-22} (\Omega\cdot cm)^{-1}$; such signal averaging is only
valid if conductivity has reached equilibrium and fluctuations
in measured currents and voltages are small and largely
uncorrelated in time.

Values for $d$ and $A$ are the time-independent and therefore
only contribute to the accuracy of the measurements [8].
Uncertainties in current dominate at lowest conductivities;
however, at conductivities $> 10^{-19} (\Omega\cdot cm)^{-3}$ typical
accuracies for sample thickness of 1% to 2% can limit the
accuracy in conductivity.

The applied electric field can affect $\sigma_{DC}$ through a field-
enhanced conductivity, which only becomes more than a ~10% effect
at applied fields >10% of the electrostatic breakdown field
[9,16]. Field-induced enhancements at ~20% of the
breakdown field strength were found to be about a factor of 2
for similar LDPE samples [9], consistent with Poole-Frenkle
theory of field-enhanced conductivity [23]. Thus,
measurements here performed at ≤32 MV/m (~5%, 12%, 16%
and 10% of the electrostatic breakdown field for LDPE, PI, PEEK
and BOPP, respectively) may introduce a small constant
increase in conductivity; however, since the drift in this applied
field is small, this will produce only a small shift in accuracy
and will not affect precision.

Fluctuations in voltage can directly affect the free electron
current transport current and the corresponding conductivity
through Eq. (3). More importantly, even very small magnitude
short-term voltage fluctuations can produce displacement
currents proportional to $dV/dt$ which are comparable to the dark
current. Even low-noise AC-to-DC power supplies have 60 Hz
and higher frequency ripples that produce larger displacement
currents [8]. A battery powered high voltage source is used here
to minimize such short-term fluctuations in voltage [13].

The voltage fluctuations for the battery voltage supply used occur
on time scales on the order of ~10^{-2} s and deviate no more than
80 ppm, making these effects on precision much less than
current-dependent uncertainties. Further, since conductivity
determinations include voltage measurements at each time step,
slow-scale voltage decay which does not produce significant
displacement current does not affect uncertainty in conductivity.
Hence, voltage measurements do not contribute significantly to the accuracy of conductivity measurements.

Contributions to precision and accuracy due to non-
equilibrium temperatures, voltages, and dose rates are also
considered here. Changes in the temperature, $\Delta T$, can manifest
in several ways. Changes in sample temperature cause direct
changes in the dark conductivity, $\sigma_{DT} \equiv \left[\frac{\sigma_{DC(T)}}{\sigma_{DC(0)}}\right] \cdot \Delta T$ (and,
previously, similarly for the polarization and transient
conductivities). This is clearly seen in the LDPE, PI, PEEK
and BOPP conductivity data, as discussed in Sec. V, and is
attributed to the small daily cyclic changes in room
temperature. On a microscopic scale, thermal shot (Johnson)
noise is produced by random motion of the constituent particles;
this contribution to the threshold for lowest measurable
conductivity is on the order of ~2·10^{-23} (Ω·cm)^{-1} for LDPE
measurements made at room temperature under 420 V [8].

Changes in voltage are largely considered above. Figure 2(b)
shows a graph of voltage and temperature versus time for long
times. Measured voltage fluctuations of the battery supply due
to diurnal temperature fluctuations in the lab are on the order of
±75 mV or ±100 ppm at ~300 mV/K. Thus, the influence of a
resulting displacement current from a typical half day
temperature rise or fall ±0.3 K the order of 7 μV/s are
negligible.

Changing dose rate can cause well-known time-dependence
in radiation induced conductivity (RIC); this includes onset RIC
for increasing dose rates and delayed RIC for decreasing dose
rates [4,16,24]. The CVC apparatus has neither artificially
applied or time-varying dose rates. However, even in a situation
with no applied dose, RIC can contribute to the threshold for
lowest measurable conductivity [8]. The small amount of
energy deposited in samples from the ubiquitous (and largely
un-shieldable) constant background dose from very high energy
cosmic radiation at sea level is ~0.26 mGy/yr [25], which

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produces a background conductivity on the order of \(3 \times 10^{-23} (\Omega \cdot \text{cm})^{-1}\) for LDPE samples and measurement methods considered here [8].

V. RESULTS AND ANALYSIS

Conductivity data as a function of time for LDPE, PI, PEEK, and BOPP are shown in Figs. 3, 4, 5, and 6, respectively. These plots also show the fit for total conductivity calculated using Eq. (3), along with individual contributions from each conduction mechanism. Values for the model parameters are given in Table I. Specific details for each of the four materials are discussed in separate sections below.

The process to determine the fitting coefficients is now described. First, \(\sigma_{\text{DC}}\) is determined by examining average currents and voltages near the end of the run. This can be complicated if the measurements were not run long enough for the sample to come to equilibrium, \(\tau_{\text{exp}} < \tau_{\text{eq}}\), as is the case for LDPE in Fig. 2(a). Complications also arise if there are significant changes in \(\sigma_{\text{DC}}\) due to diurnal changes in temperature in the lab, illustrated for LDPE and BOPP in Figs. 2(a) and 6(b), respectively. If \(\Delta \sigma_{\text{DC}} < \Delta \sigma_{\text{res}}\), these fluctuations are not seen; however, this effect is observed for all materials even at very low conductivities. It is also difficult if the dark conductivity falls below the instrumental resolution, \(\sigma_{\text{DC}} < \Delta \sigma_{\text{res}}\), as is the case for BOPP in Fig. 6. Several diurnal averages of \(\sigma_{\text{DC}}\) are taken at constant sample temperatures near the end of the run; if these values agree, the equilibrium dark conductivity can be determined.

Once \(\sigma_{\text{DC}}\) has been determined, this value is subtracted from the data, better exposing the dispersive and transitive behavior in the residual conductivity [see, e.g., Fig. 3(b)]. Finding \(\tau_{\text{transit}}\) follows easily for each material, as the time corresponding to a distinct change in slope in the residual conductivity on a log-log plot is evident. Note, it is still possible for PI to determine the kink at the longer \(\tau_{\text{transit}} = 40\) hr, despite the low transitive conductivity, \(\sigma_{\text{transit}}\), of 1.7x10^{-20} (\Omega \cdot \text{cm})^{-1}, ~25% above \(\sigma_{\text{DC}}\). Conversely for LDPE, \(\sigma_{\text{transit}}\) is over an order of magnitude higher at 5x10^{-19} (\Omega \cdot \text{cm})^{-1}, ~60% of its high \(\sigma_{\text{DC}}\) value of 8.3x10^{-19} (\Omega \cdot \text{cm})^{-1} ± 4%.

Once \(\tau_{\text{transit}}\) is established, values for the parameters \(\alpha_{\text{disp}}, \sigma_{\text{trans}}^0\), and \(\alpha\) are found for the best fit in the long time residual conductivity. Since dispersive transport theory considers \(\sigma\) as an intrinsic material property characterizing the energy distribution of localized states, efforts are made to keep \(\alpha\) the same for both dispersive and transitive conductivities.

With the time-dependent dispersive and transitive conductivity fits determined, they are also subtracted from the total conductivity, allowing the remaining residual data to be described by a polarization contribution [see, e.g., Fig. 4(b)].

The time when the sample reaches equilibrium, \(\tau_{\text{eq}}\), is when the last time-varying component of conductivity, the transitive contribution, becomes negligible. Quantitatively, this is defined here as when the transitive conductivity equals the standard deviation of \(\sigma_{\text{DC}}, \Delta \sigma_{\text{DC}}\); that is, \(\tau_{\text{eq}}\) occurs when \(\sigma_{\text{trans}} \cdot \tau_{\text{eq}}^{-1+\alpha} = \Delta \sigma_{\text{DC}}\). For example, PEEK has an uncertainty of \(\Delta \sigma_{\text{DC}} = 3 \times 10^{-21} (\Omega \cdot \text{cm})^{-1}\), where as seen in Fig. 5(a) the transitive conductivity reaches this value at ~64 hours. When PEEK—with its low \(\sigma_{\text{DC}}\)—is in equilibrium by this definition, the transitive component accounts for ~30% of the total conductivity at \(\tau_{\text{eq}}\). For materials with a higher \(\sigma_{\text{DC}}\) such as LDPE (see Table I), \(\Delta \sigma_{\text{DC}}\) has a lower fractional uncertainty associated with it, and hence the transitive conductivity has a smaller contribution of ~4% to the total conductivity at \(\tau_{\text{eq}}\).

Temperature and conductivity data of LDPE and PEEK are plotted in Figs. 2(a) and 5(b) and 5(c), respectively, with temperature and current results shown in Fig. 6(b) for BOPP. In each case (and also PI), sample temperature data has distinct diurnal fluctuations on the order of ±0.3 K over 24 h, which result from the room’s heating cycle. The dark conductivity clearly rises and falls with these temperature fluctuations. The temperature coefficient of dark conductivity, \(\sigma_{\text{DC}}^0\), can be estimated as the ratio of conductivity change to temperature change over 12 hr cycles, as listed in Table I. BOPP has the largest response to temperature, and although BOPP’s temperature coefficient is 2 orders of magnitude smaller than LDPE, the ratio of \(\sigma_{\text{DC}}^0\) to \(\sigma_{\text{DC}}\) is larger; PI and PEEK have similar \(\sigma_{\text{DC}}^0\) values. Due to the large reaction to temperature that BOPP sees, more data is needed to retrieve better values for \(\sigma_{\text{DC}}^0\).

Temperature coefficients listed in Table I are calculated in small temperature intervals of ~0.5 K, and also where temperature inflections are occurring. Figure 5(b) shows a
PEEK data set taken over a larger temperature window with a gradual cooling rate of ~2 K/hr. A linear fit has a slope of about 2 to 4 times larger than the value for $\sigma_0$ given in Table I, making values in Table I a reasonable estimate. Future data over wider temperature ranges above and below room temperature and in both heating and cooling modes (see for example ref. [26]) are needed to understand its relation to temperature and in both heating and cooling regimes to determine $\sigma_0$ more precisely.

It is testament to the resolution of the conductivity data that for LDPE the effects of a small decreasing $\sigma_{trans}(t)$ can be extrapolated to show it counterbalances increases in $\sigma_{DC}$ due to overall increasing temperature [see Fig. 2(a)]. Likewise, for PEEK the effects of small (but still decreasing) $\sigma_{trans}(t)$, extrapolated to only 10% of $\sigma_{DC}$, can be effectively removed from any changes in $\sigma_{DC}$ due to in temperature trends [see Fig. 5(c)].

The following subsections now present the results of long time scale conductivity measurements of the four polymeric materials.

A. Low-Density Polyethylene

Time-dependent conductivity data for LDPE are shown in Fig. 3(a) as a log-log plot of conductivity data over the full experiment duration of 107 hr. LDPE CVC data were acquired using an applied voltage of ~420 V, or ~17 MV/m (~9% of nominal breakdown voltage for vacuum baked samples [22]).

Fits to the total conductivity using Eq. (3) and its components are also shown in Fig. 3(a), with fitting parameters listed in Table I. The value of conductivity after only 1 hr of applied voltage at 23.9 °C, $\sigma(t = 1 \text{ hr}) = 2.6 \times 10^{-19} (\Omega \cdot \text{cm})^{-1}$, is in very good agreement with previous measurements on similar LDPE samples of $\sigma(t = 1 \text{ hr}) = 4 \times 10^{-19} (\Omega \cdot \text{cm})^{-1}$ at the same temperature and applied field [26].

The LDPE polarization amplitude, $\sigma_0$, is about the same as $\sigma_{DC}$, and is about half the magnitude of that for PEEK, BOPP, and the second $\sigma_0$ of PI. This is expected for a relatively non-polar structure like [H-C-H]n. With the polarization decay time of 144 s, the polarization contribution falls below the $\sigma_{DC}$ value at just ~12 s, and below $\Delta \sigma_{DC}$ at ~490 s.

Figure 3(b) shows a log-log plot of residual conductivity data near $\tau_{trans}$ with $\sigma_{DC}$ subtracted, along with dispersive and transitive conductivity component fits. This highlights the dispersive transport kink at $\tau_{trans} = 19.8 \text{ hr}$, and when the dispersive component reaches and falls below $\sigma_{DC}$ at ~5.7 hr. At $\tau_{trans}$ the transitive contribution has fallen to
Values for $\alpha$ for the dispersive and transitive regimes, $\alpha_{\text{disp}} = 0.6$ and $\alpha_{\text{trans}} = 0.7$, are in good agreement with the average value $\bar{\alpha} = 0.65 \pm 0.5$ in Table I and of $\alpha_{\text{disp}} = 0.62$ [26] and $\alpha_{\text{disp}} > 0.6$ [23] from previous studies.

The temperature coefficient of dark conductivity, $\sigma_0 = \frac{5 \times 10^{-19} (\Omega \cdot \text{cm})^{-1}}{K}$, can be estimated as the ratio of conductivity change to temperature change over a 12 hr cycle, as listed in Table I. This is in reasonable agreement with a previous measurement of $\frac{2 \times 10^{-19} (\Omega \cdot \text{cm})^{-1}}{K}$ [26].

### B. Polyimide

Time-dependent conductivity data for PI are plotted in Fig. 4. PI CVC data were acquired using an applied voltage of ~800 V or ~32 MV/m (11% of nominal breakdown voltage for vacuum baked samples [22]). Figure 4(a) shows the results of the entire run as a log-log plot of conductivity over the full experiment duration with the model and its constituents. This run lasted 231 hrs, significantly longer than for LDPE, although it reached equilibrium at 154 hrs, with $\sigma_{\text{dc}} = 1.5 \pm 0.3 \times 10^{-20} (\Omega \cdot \text{cm})^{-1}$. Significant noise is seen at the end of this run as the measured current approaches the limit of the instrumentation, $\Delta \sigma_{\text{es}}$. This produces some ambiguity in determining $\tau_{\text{transit}}$, which was estimated as ~40 hrs. In the case of PI, it is the transitive contribution that reduces to $\sigma_{\text{dc}}$, occurring at 44.8 hrs or about 29% of $\tau_{\text{eq}}$. PI had the largest discrepancy among $\alpha$ values, with $\alpha_{\text{disp}}$ and $\alpha_{\text{trans}}$ having values of 0.49 and 0.3, respectively; $\bar{\alpha} = 0.4 \pm 0.1$ is about 38% percent less than the value for LDPE.

The magnitude of the polarization component is larger for PI than for LDPE or other samples, and up to three orders of magnitude larger than $\sigma_{\text{dc}}$ for PI during the initial seconds. There are two polarization contributions evident in the log-linear plot of conductivity data at early times, Fig. 4(b), with $\sigma_{\text{dc}}$ and the dispersive contribution subtracted from the raw conductivity data to determine the attributes of the polarization mechanisms. The first polarization component has a large magnitude of $1.0 \times 10^{-17} (\Omega \cdot \text{cm})^{-1}$, but with a rapid decay time of 7.2 s. The second polarization component has a magnitude similar to those of all the other samples of $\sim 1 \times 10^{-18} (\Omega \cdot \text{cm})^{-1}$, and a decay time of 30.6 s, with it matching $\sigma_{\text{dc}}$ at 144 secs.

**Poly-Ether Ether Ketone**

Time-dependent conductivity data for PEEK are shown in Fig. 5(a) as a log-log plot of conductivity data over the full experiment duration of 142 hrs. PEEK CVC data were acquired using an applied voltage of ~800 V or ~32 MV/m (~16% of nominal breakdown voltage for vacuum baked samples [22]).

PEEK has a low $\sigma_{\text{dc}}$ value of $(7 \pm 3) \times 10^{-21} (\Omega \cdot \text{cm})^{-1}$, three orders of magnitude less than $\sigma_0^0$ and $\sigma_0^\text{trans}$. Even at extended time scales, the dispersive component is the main contributor to the total conductivity due to the low $\sigma_{\text{dc}}$. PEEK has the most consistent values of $\alpha_{\text{disp}} = 0.45$ and $\alpha_{\text{trans}} = 0.44$ of the four polymers, with $\bar{\alpha} = 0.445 \pm 0.005$. The polarization drops below $\sigma_{\text{dc}}$ in 63 s, which is similar to the polarizations of PI on the order of minutes. For PEEK, $\tau_{\text{transit}} = 20$ hr; PEEK’s transitive contribution falls below $\sigma_{\text{dc}}$ at 35.6 hours, about 56% of the equilibrium time, but is comparable to PI, which has a similar $\bar{\alpha}$. Equilibrium is reached at 64.1 hrs, the most rapid of the four polymers.

### C. Polypropylene

Time-dependent conductivity data for BOPP are shown in Fig. 6(a) as a log-log plot of conductivity data over the full experiment duration.
The data have a considerable response to changes in the diurnal temperature fluctuations influence on the collected material to temperature fluctuations. Additional tests need to be performed to achieve steadier data. Figure 6(a) shows the conductivity data over the full experiment duration fit using Eq. (3), which includes terms for polarization, dispersive and dark current conductivities. We can draw some conclusions about the transport process and materials characteristics.

Figure 6(b) shows current data collected of BOPP on a log-linear plot, along with the sample temperature; this emphasizes the diurnal temperature fluctuations influence on the collected data. The data have a considerable response to changes in temperature, that is exacerbated when the current data reach the electrometer's inherent background current level (red horizontal line), shown in the blue shaded region in Fig. 6(b), occurring between ~86 to ~183 hrs. When the conductivity is calculated, the background current is removed from the current data, heightening this effect and producing the results shown in Fig. 6(a), where the red line shows \( \sigma_{DC} = (5 \pm 3) \times 10^{-21} (\Omega \cdot cm)^{-1} \) at 25.7 °C, which is very similar to the conductivity resolution limit of \( \Delta \sigma_{res} = 4.9 \times 10^{-21} (\Omega \cdot cm)^{-1} \) determined by the background current level. The overall temperature increase in the red shaded region was necessary to calculate a DC value for BOPP above the resolution of our instrumentation. Taking a conductivity average over a period of data from 95-145 hours gives \( \sigma_{DC} = (3 \pm 4) \times 10^{-21} (\Omega \cdot cm)^{-1} \) at 25.7 °C, and thus the best reported value for \( \sigma_{DC} \) is less than or equal to the background conductivity value at this time interval at the reported temperature, and cannot report an equilibrium time.

VI. CONCLUSIONS

The CVC test apparatus, and in particular the use of very stable battery voltage supplies [13], is found to provide high resolution measurements of the time-dependent conductivity of HDIM. The lower limit of conductivity measured with the instrument is \( \Delta \sigma_{res} = 2 \times 10^{-21} (\Omega \cdot cm)^{-1} \), which corresponds to \( t_{\text{decay}} \) of >1 yr, for typical values of experimental parameters used here as set by the precision in the current measurements of ~1 fA. When samples reach equilibrium currents, signal averaging of measurements over 10 s can typically reduce the precision to ~1 \( \times 10^{-16} \) A and \( \Delta \sigma_{res} = 2 \times 10^{-22} (\Omega \cdot cm)^{-1} \), which corresponds to \( t_{\text{decay}} \) of >1 decade. Use of an improved electrometer with ~0.1 fA resolution is also expected to extend \( \Delta \sigma_{res} \) an order of magnitude.

The time-dependent conductivities and associated physical parameters have been determined for each of four common polymeric materials used in space applications. Ranking of \( \sigma_{DC} \) from highest to lowest is LDPE, PI, PEEK, and BOPP, although the relative contributions from the different macroscopic conduction mechanisms exhibit different ordering. In general, these results are consistent with expectations and the limited available results from previous studies. Measurements are in progress to study other polymeric and glass/ceramic HDIM. Operationally, determining smaller conductivities and longer decay times is not necessary for all but the very longest duration space missions or other applications. In addition, the enhanced sensitivity of the CVC apparatus allows study of new aspects of the transport process and materials characteristics.

Results using the CVC method for time-dependent conductivity measured over more than five orders of magnitude in time are found to be described very well by the macroscopic conductivity model for the CVC method presented in Eq. (3), which includes terms for polarization, dispersive and dark current conductivities. We can draw some conclusions about the time constants describing time-dependent conductivity from our measured results. First, the general order of the time constants listed in Eq. (4) and summarized in Table I was confirmed for all four materials, with a few minor exceptions.

Exponential decay over short time scales of 10^6 s to 10^8 s is attributed to polarization effects. These polarization terms are attributed to either interfacial or electrode polarization mechanisms found in semi-crystalline polymers [27] based on their long decay times, rather than from either electronic or atomic polarizations that occur on much shorter time scales [28]. LDPE’s \( \sigma_P^b \) has a one to two orders of magnitude lower than the other materials.
and transitive conductivity, the associated kink at well as faster polarization terms [8].

...magnitude faster or ~10^2 s; this will allow consistent measurements of other polymers; this suggests that the small polarization term observed for LDPE polymer chains, in contrast to the other polymers whose chain motion is more sterically inhibited due to more cross-linking and larger side-structures on their polymer chains. The instrumentation is being extended to include faster current measurements, up to two orders of magnitude faster or ~10^2 s, for higher currents observed in the initial 10^2 s; this will allow consistent measurements of instrumentation and charge injection behavior through \( \tau \) [9], as well as faster polarization terms [8].

The two power law time-dependent regions for dispersive and transitive conductivity, the associated kink at \( \tau \) trans, and the relative agreement between \( \alpha_{disp} \) and \( \alpha_{trans} \) confirm the predictions by Scher and Montroll based on hopping conductivity and multiple trapping models for highly disordered materials. Indeed, studies with this CVC apparatus on polymeric HDIM have remarkably extended the striking scaling characteristic of Scher-Montroll theory over more than eight orders of magnitude in time from 10^3 s < \( \tau \) transit < 10^1 s observed for amorphous semiconductors [3,11] to \( \tau \) transit \( \gtrsim \) 10^2 s for HDIM. The observed order of \( \alpha \) and \( \tau \) are the same for the four materials. This is consistent with the conjecture that large \( \tau \) is attributable to significant rearrangement of the LDPE polymer chains which could lead to a higher degree of microscopic structural disorder, a broader distribution of defect state energies, and a larger value of \( \alpha \).

Each material is found to reach (or at least approach) a well-defined constant dark current conductivity at long times, which we attribute to the non-polar nature of LDPE. Further, LDPE has an order of magnitude longer \( \tau_p \) than those observed for the other polymers; this suggests that the small polarization term observed for LDPE might be attributable to significant rearrangement of the LDPE polymer chains, in contrast to the other polymers whose chain motion is more sterically inhibited due to more cross-linking and larger side-structures on their polymer chains. The instrumentation is being extended to include faster current measurements, up to two orders of magnitude faster or ~10^2 s, for higher currents observed in the initial 10^2 s; this will allow consistent measurements of instrumentation and charge injection behavior through \( \tau \) [9], as well as faster polarization terms [8].

The two power law time-dependent regions for dispersive and transitive conductivity, the associated kink at \( \tau \) trans, and the relative agreement between \( \alpha_{disp} \) and \( \alpha_{trans} \) confirm the predictions by Scher and Montroll based on hopping conductivity and multiple trapping models for highly disordered materials. Indeed, studies with this CVC apparatus on polymeric HDIM have remarkably extended the striking scaling characteristic of Scher-Montroll theory over more than eight orders of magnitude in time from 10^3 s < \( \tau \) transit < 10^1 s observed for amorphous semiconductors [3,11] to \( \tau \) transit \( \gtrsim \) 10^2 s for HDIM. The observed order of \( \alpha \) and \( \tau \) are the same for the four materials. This is consistent with the conjecture that large \( \tau \) is attributable to significant rearrangement of the LDPE polymer chains which could lead to a higher degree of microscopic structural disorder, a broader distribution of defect state energies, and a larger value of \( \alpha \).

Each material is found to reach (or at least approach) a well-defined constant dark current conductivity at long times, although the enhanced sensitivity of the CVC tests allows subtle changes in \( \sigma_{DC} \) due to temperature and voltage fluctuations over 10^3 s time scales to be observed and quantified. A definition has been proposed for equilibration time for CVC measurements, \( \tau \) eq, after which conductivity reaches a constant \( \sigma_{DC} \). Although this definition of \( \tau \) eq depends on instrumentation...
properties through $\Delta \sigma_{res}$, it still seems to provide a better estimate of equilibrium time scales for CVC measurements than $t_{decay}$ which seems more applicable to CSC measurements. The ratio $[\tau_{trans}/\tau_{eq}] = 0.23 \pm 15\%$ is very consistent, whereas the ratio $[\tau_{decay}/\tau_{eq}]$ varies more than two orders of magnitude for the four polymers due to the added permittivity influence. The experiment durations here, $\tau_{exp}$, all exceed $\tau_{eq}$ but do not reach $\tau_{decay}$; LDPE experiments are the only exception. Note that the ratio $[\sigma^0_{disp}/\sigma^0_{trans}]$ is linearly correlated with the ratio $[\tau_{trans}/\tau_{eq}]$, with a proportionality constant $5.6 \pm 1.6$ to within the variations of these ratios amongst the four polymers; this is reasonable, as $\tau_{eq}$ is related to the ratio of $\Delta \sigma_{res}$ to $\sigma^0_{trans}$. By contrast, $\sigma_{DC}$ is not found to be correlated with $\sigma^0_{P}$, $\sigma^0_{disp}$, or $\sigma^0_{trans}$; this lack of correlation is consistent with the proposition that polarization, dispersive transport and dark conductivity are independent conduction mechanisms.

Measurements of equilibrium $\sigma_{DC}$ subject to small diurnal fluctuations in temperature as small as $\pm 0.5$ K have been used to determine values of $\sigma^0_{T}$, which are found to agree with limited results determined by other methods. Further studies will also investigate the temperature dependent dark current conductivity; these will include measurements where the temperature of materials which have reached equilibrium $\sigma_{DC}$ are slowly cycled up and down to determine T-dependent $\sigma^0_{T}(T)$ [8]. Preliminary studies of the field-enhanced conductivity [9] can now be extended to fields well below 10% of the breakdown field strength, with the enhanced sensitivity of the CVC apparatus.

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VIII. REFERENCES


