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Electrostatic Discharge and Endurance Time Measurements of Spacecraft Materials: A Defect-Driven Dynamic Model

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Measurements of Endurance Time for Electrostatic Discharge of Spacecraft Materials: A Defect-Driven Dynamic Model

Allen Andersen, JR Dennison, Alec M. Sim, and Charles Sim

Abstract—Electrostatic breakdown leads to the majority of anomalies and failures attributed to spacecraft interactions with the plasma space environment. It is therefore critical to understand how electrostatic field strength \((F_{ESD})\) of spacecraft materials varies due to environmental conditions such as duration of applied electric field, rate of field change, history of exposure to high fields, and temperature. We have developed a dual-defect, thermodynamic, mean-field trapping model in terms of recoverable and irrecoverable defect modes to predict probabilities of breakdown. Fits to a variety of measurements of the dependence of \(F_{ESD}\) of insulating polymers on endurance time, voltage ramp rate, and temperature based on this model yield consistent results. Our experimental results for the prototypical materials low density polyethylene (LDPE) and polyimide (PI or Kapton HN™) suggest that values of \(F_{ESD}\) from standard handbooks, or cursory measurements that have been used routinely in the past, substantially overestimate the field required for breakdown in common spacecraft applications, which often apply sub-critical fields for very long time periods as charge accumulates.

Index Terms—Electrostatic discharge, arcing, breakdown, spacecraft charging, space environment effects, polymers

I. NOMENCLATURE

\(a_{def}\) = mean defect separation
\(D\) = sample thickness
\(D_{bb}\) = bond breaking dose
\(E_{strain}\) = strain energy
\(F\) = electrostatic field
\(F_{def}\) = critical electrostatic field
\(F_{ESD}\) = electrostatic breakdown field
\(F_{ESD}(r_0)\) = electrostatic breakdown field at 1 V/s ramp rate
\(F_{onset}\) = onset electrostatic field for breakdown
\(h\) = Planck’s constant
\(i\) = current
\(K_{def}\) = rate of defect creation/annihilation ( +/- )
\(k_B\) = Boltzmann’s constant

\(N_{bond}\) = density of carbon-carbon bonds
\(N_{def}\) = defect density
\(N_{step}\) = number of voltage steps to reach \(V_{static}\)
\(n_{def}(t)\) = time-dependent density of occupied defects
\(p_{def}\) = probability of creating one defect
\(p_{step}\) = probability of breakdown after \(N_{step}\) voltage increments
\(P_{survive}\) = probability to survive \(N_{step}\) voltage increments
\(P_{SVET}\) = probability of breakdown for SVET test after \(\Delta t_{elapsed}\)
\(q_e\) = charge on electron
\(R_{lim}\) = resistance of current limiting resistors
\(r\) = voltage ramp rate
\(r_o\) = voltage ramp rate of 1 V/s
\(T\) = temperature
\(T_{melt}\) = melting temperature
\(t\) = time
\(t_{en}\) = endurance time to breakdown
\(V\) = applied voltage
\(V_{i}\) = applied voltage at \(i^{th}\) step
\(V_{static}\) = static applied voltage
\(\Delta t_{step}\) = elapsed time during voltage increment
\(\Delta t_{elapsed}\) = elapsed time during ESD test
\(\Delta F\) = electrostatic discharge field distribution width
\(\Delta G\) = Gibbs activation energy
\(\Delta G_{def}\) = Gibbs defect activation energy
\(\Delta V\) = activation volume
\(\Delta V_{def}\) = defect activation volume
\(\Delta V_{step}\) = voltage change during voltage increment
\(\Delta t\) = time interval field is applied
\(\beta\) = Weibull function shape parameter
\(\varepsilon_0\) = permittivity of free space
\(\varepsilon_r\) = relative permittivity
\(\nu_{def}\) = mean defect creation frequency
\(\varepsilon\) = efficiency of radiation to break bonds
\(\rho_m\) = mass density

\(s\) = Superscripts for defect type

\(A\) = type A irreversible defects
\(B\) = type B reversible defects
\(bb\) = broken bond defects
\(K\) = Kuhn pair or kink defects
\(Tot\) = total combined results for all defect types
\(S\) = single type of defects
\(W\) = estimate of defects by Weibull distribution fit

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II. INTRODUCTION

Electrostatic discharge (ESD) is the primary cause of space environment induced failures and anomalies [1]. As mission lifetimes and the sensitivity and complexity of instrumentation increase, so does the need for describing the influence of the electrical aging processes on ESD. This research studies the electrostatic field strength \( F_{\text{ESD}} \) of polymeric insulators as a function of applied field and the time-to-breakdown for applied fields less than \( F_{\text{ESD}} \). A dynamic physics-based model for time-to-breakdown in terms of breakdown probabilities is much more valuable than an empirical static model, since it provides the ability to predict the statistical lifetime of dielectric materials subjected to prolonged stress from sub-critical electric fields. Insights into spacecraft failures follow from comparison of the field-dependent endurance times with times scales relevant to the space environment and orbital conditions [2].

We present experimental results for two prototypical polymeric materials, low density polyethylene (LDPE) and polyimide (PI or Kapton HN™). \( F_{\text{ESD}} \) was determined using a custom high vacuum chamber, as a sustained rise in I–V curves. Ramp rates of \(-6 \text{ V/s}\) resulted in substantially lower \( F_{\text{ESD}} \) values than tests conducted with the maximum ramp rate of \( 500 \text{ V/s} \) recommended in ASTM D3755 standards [3]. Time-dependent breakdown was studied with different tests, by applying a static field stress less than \( F_{\text{ESD}} \) across the material and measuring the endurance time. Taken together, these suggest that values of \( F_{\text{ESD}} \) from standard handbooks or cursory measurements that have been historically used by the spacecraft charging community can substantially overestimate \( F_{\text{ESD}} \) in common spacecraft situations.

These experimental results are compared with thermodynamic mean field multiple trapping models of the electric field aging process and with available prior measurements. We introduce a first-order approximation to develop an extended dynamic temperature-dependent electrostatic discharge model that include both reversible and irreversible defect mechanisms. Reversible defect mechanisms such as bond bending or twisting have energies less than or comparable to thermal energies, so that they can be readily repaired through thermal annealing. Irreversible defects such as bond stretching or breaking have higher energies. In the proposed mean field theory, each mechanism is characterized by a mean spatial separation of sites and a mean activation energy. The model predicts the observed measurements, which show a negative logarithmic decay of endurance time to electrostatic breakdown field. This is consistent with thermodynamic models, with \( F_{\text{ESD}} \) asymptotically approaching a constant value as the time-to-breakdown goes to infinity.

We also discuss these ESD results in terms of a more comprehensive unified theory for electron transport in highly disordered insulating materials, which allows a correlation between fitting parameters and more fundamental materials properties such as atomic scale structure and bonding, mobility, transition probabilities, and spatial and energetic distributions of trap states beyond the energy mean field approximation.

III. EXPERIMENTAL METHODS

Electrostatic discharge (ESD) tests were conducted using a modified ASTM method [4,5] in a custom, high vacuum chamber (<10\^-3 Pa base pressure) [6]. Electric fields were applied to the material using a variable high voltage power supply (CPS Precision, Model 130N/1314; 0-30 kV ±2% at 5 mA) in a simple parallel plate capacitor geometry (Figs. 1 and 2). Voltage, \( V \), and current, \( I \), were monitored for the duration of the experiments using two interfaced multimeters (Amprobe®, Model 38XR-A: 100 µV and 100 nA resolution at 2 Hz acquisition rate) under LabVIEW™ control.

Samples (F, in Fig. 1) were clamped between a metal sample mounting plate (E) and six highly polished (<200 nm rms surface roughness) Cu high voltage electrodes (G). This allowed testing of six samples during a single vacuum cycle. A spring clamping mechanism (A) was employed to apply uniform sample contact pressure of ~0.4 MPa, in compliance with standard methods [4].

Three types of ESD measurements were made: dynamic incremental-voltage breakdown (step-up) tests (see Fig. 4(a)), static voltage endurance time (SVET) tests (see Fig. 4(b)), and temperature-dependent step-up measurements. All three types of measurements began by incrementing the applied voltage at \( V_{\text{step}} \approx 20 \text{ V} \) at \( \Delta t_{\text{step}} \approx 3.5 \text{ s} \) time intervals (more precisely, on a cycle of three \( \pm 1 \text{ V} \) increments at 3.00±0.02 s intervals followed by one \( 33\pm1 \text{ V} \) increment at a 4.00±0.02 s time interval) up to 30 kV (blue regions in Fig. 3). For step-up tests (see Fig. 3(a)), the voltage was increased incrementally at constant rate until complete breakdown occurred. For step-up
measurements, current increased significantly at breakdown (typically up to on the order of 10 μA) and continued to rise linearly above breakdown, with a slope set by the sum of the residual sample resistance and two in series current limiting resistors ($R_{sw}=100\,\text{MΩ}$ in Fig. 2).

Static voltage endurance time (SVET) measurements of the endurance time, $t_{en}$, of electrostatic breakdown (see Fig. 3(b)) were conducted by similarly incrementing the applied voltage to a plateau voltage, $V_{static}$, and then maintaining this static electric field across the sample until complete electrostatic breakdown occurred. Typical static voltages for the endurance time experiments described here were in the range of 4 kV to 9 kV. These values yielded endurance times from a few minutes to a few days. The appropriate value of the endurance time, as determined from the elapsed time as logged by the data acquisition program measured from when the initial voltage was applied, is discussed in Section V.B.

Temperature-dependent measurements were conducted over a range from ~150 K to 325 K. Measurements were made by cooling samples in thermal contact with an aluminum liquid nitrogen filled cryogen reservoir (C). Temperature was monitored with Type K thermocouples attached to two Cu temperature sensors (H) in good thermal contact with the sample, but electrically isolated (I). Temperatures typically increased less than 0.6 K/min or $\lesssim 15$ K during a single cryogenic step-up testing cycle.

Samples of branched LDPE used in studies described here ([3,7], ASTM D-5213 type I) of 29.7±2% μm average measured thickness ($\lesssim 2\%$ average thickness variation for any one sample) had a density of 0.92±0.01 g/cm$^3$ [7] with an estimated crystallinity of 50% [8], an estimated peak fractional mass distribution of $\sim 6\cdot10^3$ amu or $\sim 2\cdot10^3$ C$_3$H$_4$ mers per chain [6,9], and a relative dielectric constant of 2.26 [7]. Samples of Kapton HN™ ([3,10], ASTM D-5213 type I) of 23.9±4% μm average measured thickness (3% average thickness variation for any one sample) had a density of 1.43±0.01 g/cm$^3$ [10], and a relative dielectric constant of 3.5 [10]. A single mer of Kapton HN™ has an atomic composition of C$_{22}$O$_2$N$_2$H$_10$ [10].

All samples were chemically cleaned with methanol prior to a bakeout at 338±1 K under $\sim 10^{-3}$ Pa vacuum for ~24 hr, while in contact with a grounded surface to eliminate absorbed water and volatile contaminants and any residual stored charge; samples conditioned in this manner had a measured outgassing rate of $<0.05\%$ mass loss/day at the end of bakeout, as determined with a modified [6,11] ASTM 1559 [12] test procedure.

IV. THEORY

Electrical aging or stress (prolonged exposure to high electric fields) can cause breakdown in insulating materials. Aging in the spacecraft environment is induced by high energy particle flux into or through a material, by medium to high applied electric fields, or by contact carrier injection [2]. Numerous studies have shown that electrical aging can be characterized by (i) the density of defects created within the material from bond stress due to local and applied electric fields and (ii) the Gibbs free energy, bond destruction energy, or cohesion energy associated with creation of these defects [13-17].

A. General Breakdown Theory

To understanding how the bonds within a polymeric material are affected by an applied stress due to internal or external electrostatic fields, consider an electric field $F$ across two faces of a cubic unit volume acting as a parallel plate capacitor. The stain energy required to compress this unit volume by an amount $\Delta V$ is [18]

$$E_{strain} = \frac{1}{2}\varepsilon_0\varepsilon_r F^2\Delta V. \quad (1)$$

More detailed vector or tensor calculations of the strain energy for more realistic, anisotropic shapes yield similar results that differ only by a constant of order unity. Alternate theories [8,12,14-17], which produce equivalent results, consider the energy, $q_aF$, acquired by a charge carrier with charge $q_a$ as it moves through a mean field, $F$, over a mean separation distance between defects, $a$; to account for the dielectric response of the material, the carrier charge density is replaced with $(q_a/a^2) = \frac{1}{2}(\varepsilon_0\varepsilon_r F)$.

Now consider a density of defects—e.g., ionization sites or broken bonds—associated with electrostatic discharge, $N_{def}$, and a cubic mean activation volume, $\Delta V_{def}=(a_{def})^3\equiv I/N_{def}$, associated with one such defect. For comparison, in LDPE the approximate density of C$_3$H$_4$ mers is $\sim 2\cdot10^{22}$ cm$^{-3}$, polymer chains is $\sim 8\cdot10^{18}$ cm$^{-3}$, and crystalline lamella is $\sim 10^{15}$ cm$^{-3}$ based on measured physical properties of the material. If we set the strain energy of Eq. (1) in a volume $\Delta V_{def}$ equal to the Gibbs defect activation energy $\Delta G_{def}$, we can solve for the critical electric field, $F_{def}$, just strong enough to produce one defect per activation volume:

$$F_{def} = \left[(2/\varepsilon_0\varepsilon_r) N_{def}\Delta G_{def}\right]^{1/2}. \quad (2)$$

For permanent defects, the critical field represents a mean electrostatic field energy density large enough that on average defects are generated in every activation volume and breakdown is complete. At fields somewhat below the critical field, one can envisage interconnected regions of defective
activation volumes—that have essentially undergone an insulator-to-conductor transition—that allow current to propagate through the material via a percolation-like network. Such a percolation-like model lends itself to a decrease in (but still finite) probability of breakdown with decreasing field—as the probability of completing a percolation path across the sample at a given defect density decreases; this also predicts an onset field, $F_{\text{onset}}$, at the percolation threshold for defect densities below which breakdown will not occur. For processes that permit repair of the defect, dynamic percolation models need to incorporate defect activation volumes with a finite lifetime. Estimates of the defect activation energies and defect densities for the samples studied here, and the associated critical and onset fields, are presented in Section IV.C where they are compared with measured results.

B. Endurance Time Equation

Given a model for the critical field, a thermodynamic model for the electric field aging process has been developed to predict the mean time to failure or endurance time, $t_\text{en}$, as a function of high electric field and temperature [15,17,19-21]. There are direct equivalences between the thermodynamic model for ESD and Mott’s model for thermally activated hopping conductivity [22]. As with this conductivity model, $\Delta V_{\text{def}}$ and $\Delta G_{\text{def}}$ represent a mean defect activation volume (or barrier width) and a mean defect activation energy (or barrier height of the energy well), respectively (see Fig. 4(a)) [8,23].

On average the forward and backward movements of charge carriers from one trap state to an adjacent site can be thought of as a rate process, where motion with (against) the field corresponds to the mean uncertainty for a broken bond $h/\Delta t$ and $P_{\text{def}}^n$ [20]:

$$P_{\text{def}}(\Delta t, F, T) = \left(\frac{2k_B T}{\hbar / \Delta t}\right) \exp\left[-\frac{\Delta G_{\text{def}}}{2k_B T}\right] \sinh\left[\frac{\varepsilon_r \varepsilon_0 F^2}{2k_B T N_{\text{def}}^{\Delta G_{\text{def}}}}\right].$$ (3)

The development of Eq. (3) is reminiscent of the early hopping conductivity work of Miller and Abrahams [24].

The probability to create one defect per unit volume $\Delta V_{\text{def}}$ is equal to unity at the endurance time, $P_{\text{def}}(\Delta t=t_\text{en})=1$. $P_{\text{def}}(t_\text{en})$ corresponds to the mean defect creation frequency, $v_{\text{def}}$; thus, $h/\Delta t=h/t_\text{en}$ can be thought of as the quantum energy uncertainty for a broken bond or $P_{\text{def}}$ as the probability of tunneling through the barrier in Fig. 4. Solving Eq. (3) with $P_{\text{def}}=1$ for the endurance time to breakdown under an applied field, we find

$$t_{\text{en}}(F, T) = \left(\frac{\hbar}{2k_B T}\right) \exp\left[\frac{\Delta G_{\text{def}}(F, T)}{k_B T}\right] \csc\left[\frac{\varepsilon_r \varepsilon_0 F^2}{2k_B T N_{\text{def}}^{\Delta G_{\text{def}}}(F, T)}\right].$$ (4)

The defect activation energy $\Delta G_{\text{def}}$ and the number density of defects $N_{\text{def}}$, are the field- and temperature-dependent fitting parameters of the model. $\varepsilon_r$ is the relative dielectric constant and a property of the material. Planck’s constant $\hbar$, the Boltzmann constant $k_B$, and the permittivity of free space $\varepsilon_0$ are fundamental physical constants. The applied field $F$ and
temperature $T$ are independent variables that can be changed with each measurement.

Alternately, one can consider material breakdown as a function of the number of occupied defects, $n_{def}(t)$. The rate of net defect creation is equal to the difference of two terms—the first for defect creation and the second for defect repair—each of which is the product of the number of sites for defect formation (or annihilation) times a defect creation (or annihilation) rate function:

$$\frac{dn_{def}(t)}{dt} = [N_{def} - n_{def}(t)] \cdot K_{def}^+(F, T) - n_{def}(t) \cdot K_{def}^-(F, T).$$  \hspace{1cm} (5)

This model [25], based on rate theory and the idea that the defect formation or bond breaking kinetics should be similar to kinetic rate reactions in chemical systems, provides a way to calculate the increase in defect density as a function of time and temperature. An expression for the rate at which defect creation ($K_{def}^+$) and annihilation ($K_{def}^-$) occurs is

$$K_{def}^\pm(F, T, t) = \frac{k_B T}{h} \exp \left[ -\frac{\Delta G_{def}^{\pm} \pm \frac{1}{2} F(t)^2 \varepsilon_r \varepsilon_0 \Delta V_{def}^{i}}{k_B T} \right]$$

using Eq. (2) and the relation $\Delta V_{def} = 1/N_{def}$. Note Eq. (6) follows directly by equating $K_{def}^\pm$ to the time derivative of Eq. (3). Here, $\pm$ refers to motion of negative charge carriers with or against the field. Also note that the rate functions, $K_{def}^\pm$, can be—and usually are—functions of both applied field and temperature. They can also be time dependent through a time-dependent component of the internal electric field from the accumulation of charge within the material or a time-dependent defect density, $N_{def}(t)$.

Using Eqs. (5) and (6), one can recover the results in Eq. (3) and show that $P_{def}(t) \propto \Delta t \left( \frac{dn_{def}(t)}{dt} \right)^{-1}$. Equation (5) suggests an important connection between the rate of bond breaking and resulting creation of electron traps. In particular, it can be shown using a multiple trapping transport theory [26] that the solution to Eq. (5) for the number of bonds broken as a function of time, temperature, and applied field is consistent with impact ionization rate equation models proposed by Kao [13]. This connection suggests that for studies involving the configuration shown in Fig. 2, but for applied fields normally considered safe, many materials will fail after very long exposure to intermediate fields. This behavior has been observed in many polymers and other highly disordered insulating materials.

Tmka [27] discusses the basic Crine model [15,19] that we extend and emphasizes the importance of improvements to endurance theory coupled with accelerated laboratory testing. Czaszjko [28], Griffiths [21], Dang [29], and Dissado and Fothergill [17] review alternate theories relating the endurance time to the electrostatic breakdown and temperature, such as the more simple inverse power law model [17] and the more complete electrokinetic endurance model [29,30] that predicts a threshold value for electrostatic breakdown at long endurance times. All these theories predict roughly similar values for endurance and approximately similar temperature dependence in the range of endurance times typically measured by experimental tests, that is, in the range of $10^6$ to $10^9$ s [29].

**C. Defect Mechanisms**

We turn our attention now to specific processes involved in ESD to establish relevant values for $N_{def}$ and $\Delta G_{def}$. Consider two types of breakdown processes, Types A and B, as illustrated in Figs. 5(a) and 5(b), respectively. Type A processes are lower energy irreversible process, that have a significant rate of defect repair. Type B processes are higher energy largely irreversible processes, with a negligible defect repair rate, at relevant temperatures. In Type B viscous or inelastic deformation processes, breakdown of the material is due to direct stress on molecular segments causing irreparable damage with no bond repair possible [31], where the ends of broken bonds with unpaired sites can act as electron traps [13,19,30]. In these processes, there is little ionization or segmental motion. Such defects can be generated by the breaking of carbon-carbon bonds of the C\(_2\)H\(_4\) monomer alkane single bonds along polymer chains, with dissociation energy $\Delta G_{def}^{bb} = 3.65$ eV/bond [32]. We can expect similar values of $\Delta G_{def}^{bb}$ for many polymers, due to the similarity in carbon-carbon bonds in their polymer chains. The energy distribution for the deep level defects should be fairly narrow since the bonds are relatively homogeneous. $\Delta G_{def}^{bb}$ will be largely independent of the environment surrounding the bond and should not depend on the orientation.

![Fig. 4. Potential energy versus position with (top) no electric field and (bottom) electric field. The field stress acts to reduce the energy necessary to initiate the degradation process through thermally assisted tunneling from the defect energy (Gibbs energy of activation, $\Delta G_{def}$) by an amount $\frac{q}{2}a_0 F$, where $a_0$ is the mean defect separation. The red curves are the carrier potential and the blue dashed curves are the field energy, as functions of position.](image-url)
of the bond with respect to the field since it is an impact ionization process creating a point defect. The bond breaking process will not have a significant temperature dependence at accessible temperatures below the melting temperature $T_{\text{mol}}$ or decomposition temperature, since $k_{\text{B}} T < k_{\text{B}} T_{\text{mol}} \Delta G^*_{\text{def}}$, hence $K^+_{\text{def}}$ will not be temperature or field dependent and $K^-_{\text{def}}$ will be negligible.

The total density of such bonds can be estimated from the mass density of LDPE and the mass of the mer (assuming one bond per mer) to be $N_{\text{bond}} \leq 4 \cdot 10^{12}$ bonds/cm$^3$. The density of broken bonds at complete breakdown can be estimated from radiation damage studies as $N_{\text{def}}^{bb} \leq \left[ \frac{1}{2} D_{bb} \rho_m \Xi / \Delta G^*_{def} \right] \approx 1.5 \cdot 10^{18}$ broken bonds/cm$^3$, where: (i) the dose (deposited energy—from the field or from incident electron radiation—per unit mass) at breakdown $D_{bb} \approx 2 \cdot 10^5$ Gy, since irradiation damage radiation damage (e.g., electron transport and emission properties) typically occurs for doses $\geq 10^5$ Gy [33,34] and mechanical failure occurs at $\geq 10^6$ Gy [35]; (ii) from radiation damage experiments, the mean energy required to break such a bond is $\Delta G^*_{def} / \Xi \approx 130$ eV [36]; and (iii) the efficiency of radiation to break bonds, $\Xi \approx 36$ [36]. This independent estimate of broken bonds in the amorphous region $\leq [D_{bb} \rho_m \Xi / \Delta G^*_{def}] \approx 7.5 \cdot 10^{18}$ broken bonds/cm$^3$ is consistent with the estimated density of chains, $1.5 \cdot 10^{18}$ broken bonds/cm$^3$ (see Section IV.A), since there is one broken bond per chain. Note, both $N_{\text{bond}}$ and $N_{\text{def}}^{bb}$ should be reduced by $\approx \frac{1}{2}$, since ESD is limited to transport across amorphous regions and $N_{\text{def}}^{bb}$ is further reduced by a factor of $\frac{1}{2}$ when a percolation threshold in the amorphous region is taken into account [37]. The value obtained, $N_{\text{def}}^{bb} \approx 1.5 \cdot 10^{18}$ cm$^{-3}$, is consistent with a range of published values for LDPE near $1-3 \cdot 10^{18}$ cm$^{-3}$ [6,38]. Since $N_{\text{bond}} \gg N_{\text{def}}^{bb} > n_{\text{def}}^{bb}(t), n_{\text{def}}^{bb}(t)$ is negligible in the first term of Eq. (5). Taken together, these estimates, in conjunction with Eq. (2), lead to a critical field for broken bond defects of $F_{\text{def}}^{bb} \approx 295$ MV/m, with $N_{\text{def}}^{bb} \approx 1.5 \cdot 10^{18}$ broken bonds/cm$^3$ and $\Delta G^*_{def} \approx 3.65$ eV/bond.

Type A processes are reversible; that is, they require a low enough activation energy that such defects can be spontaneously repaired due to thermal activation. These can include weak van der Waals bonds and main chain reconfiguration energies such as chain rotations and kinks. Creation of such defects in molecular or crystalline segments of the polymer chains result either from charge injection and impact ionization or from conformational defect (kink) generation [13]. As the injected charge becomes trapped at these defect sites in the ionized molecular segments and on chain segments, a high localized field develops leading to breakdown.

We consider one potential type of reversible defects further, kink defects. Trans-gauche rotational barriers for typical isolated longer alkane chains are 0.36 eV/kink. In polymers, close proximity of other chains leads to chain-chain interactions and steric hindrance that limits kink formation. It is often found that formation of two kinks in close proximity (which minimize displacement of the overall chain) are energetically more favorable than formation of a single kink and the concomitant large displacement of the rest of the chain. This is referred to as formation of a Kuhn pair, with a minimum kink separation (Kuhn length) of ~3.5 C-C bond lengths (~1.3 nm) for LDPE [18]. A very crude estimate of the magnitude of this effect is based on the ~25% increase in maximum working temperatures of cross-linked polyethylene over low density polyethylene. We can therefore estimate the defect energy as approximately twice the kink formation energy plus ~25% additional energy to account for chain-chain interactions and steric hindrance: $\Delta G^*_{def} \approx (1.25 \cdot 2.0-0.36$ eV/kink)$=0.90$ eV. An upper bound on $N_{\text{def}}^{K}$ can be estimated as $\approx 14\%$ of the mer density (see Section IV.A), $N_{\text{def}}^{K} < 3 \cdot 10^{21}$ Kuhn pairs/cm$^3$; this assumes a minimum separation of Kuhn pairs to the minimum kink separation of 3.5 mers and that only ~50% of the total chains can contribute, since only chains in the amorphous region are free to develop kinks unhindered. Using these same approximations for polyimide, with a working temperature ~75% above LDPE [10], minimal crystallinity, and a Kuhn length of ~8 nm [39], predicts $\Delta G^*_{def} \approx 1.3$ eV and $N_{\text{def}}^{K} < 5 \cdot 10^{20}$ Kuhn pairs/cm$^3$.

We can expect that $\Delta G^*_{def}^{K}$ will be substantially different for different polymers, due to strong variations in the chain structure, rigidity and crosslinking. The energy distribution for these defects should be broader, since the local chain environments are not homogeneous. $\Delta G^*_{def}^{K}$ should depend on the orientation of the bond with respect to the field, since this provides the torque to reorient the chains. The applied field has a well-defined direction; however the field due to internal charge accumulation will be largely isotropic and will not provide net torque. There may even be a saturation effect, as more kinks develop to align the chain segments in the disordered regions with $F$ or as bond breaking becomes prevalent producing shorter chains which align more easily with the field. The kink formation process will also have a significant temperature dependence at accessible temperatures below the melting temperature or decomposition temperature. Thermal annealing may also act to reduce the equilibrium defect density for these lower energy defects. Hence $K^+_{def}$ will be both temperature and field dependent and $K^-_{def}$ will not be negligible.
V. ELECTROSTATIC BREAKDOWN MEASUREMENTS

A. Dual Mechanism Model Fit to Data

Figure 6 shows the measured data for time to breakdown as a function of applied field for LDPE endurance time tests for the data acquired at 20 V per 3.5 s ramp rate to a static voltage. There are data from 55 step-up tests shown, which took a total of 272 hr acquisition time. Measured endurance times conducted at electric fields from 180 to 290 MV/m spanned almost five orders of magnitude in time from ~10 s to several days. The colored bars on the right axis indicate the time scales in larger units. Error bars in time for the data are less than the size of the symbols, except as shown at $t_{\text{on}} = 1$ s. Error bars in electric field are largely determined by the ~2% variations in film thickness.

There is a definite transition between two separate field regimes evident in Fig. 6, suggesting that a new composite model is required which incorporates at least two defect mechanisms. The data below ~270 MV/m with endurance times on the order of a few hours to several days were dominated by the recoverable processes and can be fit (blue dashed curve) by Eq. (4) with $\Delta G_{\text{def}}^A = 0.95$ eV and $N_{\text{def}}^A = 7 \times 10^{21}$ cm$^{-3}$. The data above ~270 MV/m with endurance times on the order of ~10 s to ~1 hr. can also be fit (red dashed curve) separately by Eq. (4) with $\Delta G_{\text{def}}^B = 3.65$ eV and $N_{\text{def}}^B = 1.5 \times 10^{18}$ cm$^{-3}$. The dual mechanism multiple trapping model (black line Fig. 6) equates the total probability of failure from either type of defect to the sum of failures for both Type A and Type B processes:

$$P_{\text{tot}}(\Delta t, F, T) = \sum_{i=A,B} P_{\text{def}}^i = \left( \frac{2k_BT}{h/\Delta t} \right) \sum_{i=A,B} \exp \left[ -\Delta G_{\text{def}}^i \right] \sinh \left[ \frac{\epsilon_r \epsilon F^2}{2 N_{\text{def}}^i k_BT} \right].$$

This assumes the probabilities $P_{\text{def}}^A$ and $P_{\text{def}}^B$ are independent of the other defect type. Once again, to find $t_{\text{on}}$, we set $P_{\text{def}}^{\text{tot}} = 1$ in Eq. (7) and solve for $t_{\text{on}} = \Delta t$. Thus,

$$t_{\text{on}}(F, T) = \left( \frac{h}{2k_BT} \right) \sum_{i=A,B} \exp \left[ -\Delta G_{\text{def}}^i \right] \sinh \left[ \frac{\epsilon_r \epsilon F^2}{2 N_{\text{def}}^i k_BT} \right]^{-1}.$$  

The values for the fitting parameters are in excellent agreement with the values predicted in Section IV.C. For Type B irreparable defects, $\Delta G_{\text{def}}^B$ and $N_{\text{def}}^B$ agree with the predicted values $N_{\text{def}}^B \approx 1.5 \times 10^{18}$ broken bonds/cm$^3$ and $\Delta G_{\text{def}}^B = 3.65$ eV/bond. For Type A reparable defects, $\Delta G_{\text{def}}^A$ and $N_{\text{def}}^A$ agree with the predicted values $N_{\text{def}}^A \approx 3 \times 10^{20}$ Kuhn pairs/cm$^3$ and $\Delta G_{\text{def}}^A = 0.90$ eV. Errors in the fitting parameters are estimated by assuming a ±5% deviation in the values of $\Delta G_{\text{def}}^A$ and $\Delta G_{\text{def}}^B$ used in Eq. (8) to produce the blue curves in Fig. 6; these show a maximum deviation in the endurance time of ~1 order of magnitude consistent with a spread in the measured data.
B. Correction for Ramping Time

Note that the endurance time used to generate the black curve in Fig. 6 is approximated as the elapsed time at the static field, and does not include the ramping (step-up) time. At short elapsed times this overestimates the endurance time. However, this is significant only for endurance times comparable to or less than ramp times of ~20 min, where the dotted line in Fig. 6 showing ramping time to a given field for the data acquired at 20 V per 3.5 s crosses the endurance curve. The inset in Fig. 6 shows the influence of the ramping process on the measured time to breakdown: the black curve assumes no contribution from the ramping process, the yellow curve assumes each ramp step field places as much stress on the material as the static field, and the green curve weights each ramp time interval with the appropriate field dependent failure probability (see Eq. (12) derived below). Note that even at high fields, the discrepancy in $F_{ESD}$ between the correct (green) curve and the approximate (black) curve is <5% at $t_e=1$ s and is <20% of the variation due to ±5% uncertainties in the defect energies at $t_e=1$ s. Error bars in time for the data are less than the size of the symbols, except as shown at $t_e<200$ s.

We now develop the correction for ramping time from probability considerations. The probability to break down when exposed to a field $F$ for a time $\Delta t$ is given by Eq. (3) or Eq. (7); the probability of survival is $[1-P_{\text{fail}}(\Delta t, F, T)]$. The probability to survive $N_{\text{step}}$ incremental voltage steps of $\Delta V_{\text{step}}$ volts, each for a time $\Delta t_{\text{step}}$ up to a static voltage $V_{\text{static}}=N_{\text{step}}\Delta V_{\text{step}}$ is the product of the survival probabilities of each increment:

$$P_{\text{survive}}^{\text{tot}}(\Delta t_{\text{step}}, N_{\text{step}}, \Delta V_{\text{step}}, T) = \prod_{j=1}^{N_{\text{step}}} \left[ 1 - P_{\text{fail}}^{\text{tot}}(\Delta t_{\text{step}}, \frac{j \Delta V_{\text{step}}}{D}, T) \right].$$

The complementary probability of breakdown, $P_{\text{step}}=(1-P_{\text{survive}})$, is:

$$P_{\text{step}}^{\text{tot}}(\Delta t_{\text{step}}, N_{\text{step}}, \Delta V_{\text{step}}, T) = 1 - \prod_{j=1}^{N_{\text{step}}} \left[ 1 - P_{\text{fail}}^{\text{tot}}(\Delta t_{\text{step}}, \frac{j \Delta V_{\text{step}}}{D}, T) \right].$$

Equation (12) yields the corrected green curve in the inset of Fig. 6.

C. Ramp Rate Dependence

Equation (12) yields the corrected green curve in the inset of Fig. 6.

A closely related question is how measured breakdown depends on the ramp rate up to a given voltage. Step-up tests were conducted on Kapton E samples. Ramp rate dependence was investigated by varying the rate of incremental voltage steps to reach electrostatic breakdown. Figure 8 shows slower ramp rates (as low as 20 V steps at 3.5 sec intervals) resulted in >35% lower $F_{ESD}$ values than tests conducted at the maximum ramp rate of 500 V/s recommended in ASTM standards [5].

This effect can be estimated by assuming that only the applied field during the final step-up contributed to the breakdown (equivalent to the yellow curve of Fig. 6), setting the ratio of Eq. (3) evaluated at $\Delta t = 1$ s and $\Delta t = \Delta t_{\text{step}}$ equal to the ratio of the experimental ramp rate $r$ to $r_0$, and using the relation $\arcsin(x) = \ln(x + \sqrt{1 + x^2})$. The ramp dependent electric field strength is
The literature and the theoretical discussions above suggest that ESD is a stochastic process rather than an asymptotic breakdown during the step up time produces a finite asymptotic limiting field as the ramp rate becomes very small, rather than approaching zero field as predicted by Eq. (13).

D. Statistical Analysis of Breakdown Field Strength

The literature and the theoretical discussions above suggest that ESD is a stochastic process [13,15,20,30,40], Fig. 9 shows the percent of samples broken down versus breakdown field during 89 LDPE and 36 Kapton step up tests (see Section III). The step up data are fit (black solid curves) with the two parameter Weibull distribution for the probability of failure [29,39,40]:

\[ P_{\text{def}}^W (F) = 1 - \exp \left( -\left( \frac{F}{F_{\text{def}}} \right)^\beta \right) . \] (14)

The Weibull scale parameter, \( F_{\text{def}}^W \), defined as the field corresponding to a 63.2% breakdown cumulative probability, approximates the field associated with the defect energy involved in breakdown. \( \beta \) is the Weibull shape parameter.

For LDPE \( \beta = 6.96 \), in agreement with results Chauvet and Laurent for similar materials of \( \beta = 6.6 \) [40]. For Fig. 9(a), \( F_{\text{def}}^W = 293 \) MV/m; comparison of \( F_{\text{def}}^W \) is difficult due to ~10 times faster ramp rate and 10 times thicker samples for the Chauvet and Laurent study [40,41]. For Kapton \( \beta = 10.9 \), in rough agreement with a range of 8 \( \leq \beta \leq 22 \) for similar polyimide films [42]. For Fig. 9(b), \( F_{\text{def}}^W = 336 \) MV/m.

Based on the probabilistic interpretation of the Weibull distribution, we define the onset of breakdowns, \( F_{\text{onset}} \) as \( P_{\text{onset}}^W (F_{\text{onset}}) \approx 0.0455 \) or 2\( \sigma \) below \( F_{\text{def}}^W \). Likewise, we define the field by which we expect most breakdowns to occur, \( F_{\text{ESD}} \).

At slower ramp rates the first approximation breaks down (see Fig. 7). Properly accounting for the probability of breakdown during the step up time produces a finite asymptotic limiting field as the ramp rate becomes very small, rather than approaching zero field as predicted by Eq. (13).

Both data sets were fit to Eq. (10) which can also be used to fit the data in Fig. 9.

\[ F_{\text{onset}}^W \text{ to } F_{\text{def}}^W \text{ defines the blue region, } F_{\text{def}}^W \text{ to } F_{\text{ESD}}^W \text{ defines the yellow region and fields above } F_{\text{ESD}} \text{ are colored in red. For } \text{LDPE } F_{\text{onset}}^W = 189 \text{ MV/m and } F_{\text{ESD}}^W = 345 \text{ MV/m. For Kapton } F_{\text{onset}}^W = 253 \text{ MV/m and } F_{\text{ESD}}^W = 373 \text{ MV/m.}

Closer inspection of the Weibull fits to Figs. 9(a) and 9(b) show a consistent discrepancy, with the fit mostly over predicting the breakdown below \( F_{\text{def}}^W \) and largely under predicting the breakdown above \( F_{\text{def}}^W \). The low field data for LDPE in Fig. 9(a) are fit well with one Weibull distribution and the high field data are fit well by a second Weibull distribution. Similar evidence for low- and high-field Weibull distributions have been noted for polyimide [42] and polypropylene [43] films, as discussed in [17].

The dual-mechanism nature of the polymers is modeled by Eq. (10), which can also be used to fit the data in Fig. 9. The orange dot-dashed curve in Fig 9(a) is \( P_{\text{tot}}^W \) from Eq. (10) using values of \( \Delta G_{\text{def}}^A, N_{\text{def}}^A, \Delta G_{\text{def}}^B \), and \( N_{\text{def}}^B \) from our fit to SVET data (Fig. 6). Although this fit exhibits the approximate shape of the distribution, it is not a good fit to the data. A fit to LDPE step up data using Eq. (10) with four adjustable parameters was also attempted (not shown) without improved accuracy.
parameters yields similar values for Type A defects ($\Delta G_{\text{def}}^{A} = 0.95$ eV, $N_{\text{def}}^{A} = 2.8 \times 10^{21}$ cm$^{-3}$), but significantly different values for Type B defects ($\Delta G_{\text{def}}^{B} = 1.07$ eV, $N_{\text{def}}^{B} = 3.15 \times 10^{19}$ cm$^{-3}$). This dual-mechanism fit (blue dotted curve), which is the sum of contributions from Type A defects (black dot-dashed curve) and Type B defects (green dot-dashed curve), is a very good fit to the data. At this point, the discrepancies for the Type B defect parameters, particularly the defect energy, are not understood. This difference could be indicative of another defect mechanism or perhaps results from an approximation in our derivation of Eq. (10), for instance that $N_{\text{def}}^{B}$ is constant. We do note that the crossover field, $\approx 275$ MV/m, between $P_{\text{step}}^{A}$ and $P_{\text{step}}^{B}$ (the intersection between the grey and green dashed curves in Fig. 9(a)) is essentially the same as the crossover field for the intersection between $t_{\text{en}}^{A}$ and $t_{\text{en}}^{B}$ (blue and orange dashed curves in Fig. 6).

E. Temperature Dependent Processes

The temperature dependence of $F_{\text{ESD}}$ of thin film insulators has been studied with step-up tests conducted over a range of fixed temperatures from $\sim 150$ to $300$ K (see Fig. 10). A small linear temperature dependence of $F_{\text{ESD}}$ for LDPE was observed in the range of 150 K to 240 K. There was an abrupt change to a nearly temperature-independent behavior above $\sim 240$ K. These data are consistent with higher temperature measurements by Shinyama [36] who observed a roughly temperature-independent breakdown field strength of $\sim 450$ MV/m over 295 K to 330 K at 1kV/s ramp rates for similar 25 µm thick LDPE samples; $F_{\text{ESD}}$ then decreased linearly to $\sim 250$ MV/m at 385 K. The 1.6X ratio of Shinyama’s $F_{\text{ESD}}=450$ MV/m at 1kV/s rate with the $F_{\text{ESD}}=280$ MV/m at 5.7 V/s in Fig. 10 is consistent with the ratio of 1.8X for similar ramp rates in Fig. 8.

Values for the dominant defect energy and density can be determined from linear fits to the temperature data in Fig. 10. By setting Eq. (3) at breakdown where $P_{\text{def}}(\Delta t = t_{\text{en}}) = 1$ for two temperatures, $T_{1} < T_{2}$, assuming $\Delta G_{\text{def}}$, $t_{\text{en}}$, and $N_{\text{def}}$ are approximately constant over $T_{1} < T < T_{2}$, and using the approximation $\sinh(x) = x$, we find a temperature-independent $\Delta G_{\text{def}}$ from the slope as

$$
\Delta G_{\text{def}}^{T} = \frac{k_{B}}{\left(T_{2}^{-1}-T_{1}^{-1}\right)} \ln\left[F_{\text{def}}(T_{2})^{2} - F_{\text{def}}(T_{1})^{2}\right]
$$

and then a temperature dependent $N_{\text{def}}^{T}$ from the value of $F_{\text{ESD}}$ at each temperature as

$$
N_{\text{def}}^{T} = \frac{\varepsilon_{\text{def}}}{2} \left[F_{\text{def}}(T)^{2}/\Delta G_{\text{def}}^{T}\right].
$$

For the low temperature branch of Fig. 10 we find $\Delta G_{\text{def}}^{LT} = 1.5$ eV and $N_{\text{def}}^{155K} = 2.4 \times 10^{18}$ cm$^{-3}$ and $N_{\text{def}}^{235K} = 5.7 \times 10^{18}$ cm$^{-3}$. For the high temperature branch, $\Delta G_{\text{def}}^{HT} = 4$ eV and $N_{\text{def}}^{240K} = N_{\text{def}}^{293K} = 1 \times 10^{18}$ cm$^{-3}$; the values for these parameters at high temperature are consistent with room temperature values estimated from other methods in this study.

The observed transition in electric field strength in LDPE may be related to a LDPE structural phase transition observed at between 250 K and 262 K. This $\beta$ transition is routinely observed in branched polyethylene, and has been associated with conformational changes along polymer chains in the interfacial matrix of disordered polymers between nanocrystalline regions in the bulk. Similar abrupt (often discontinuous) changes near $\sim 250$ K have been seen in prior studies of mechanical and thermodynamic properties and electron transport properties including dark current conductivity [23,38], radiation induced conductivity [23,44,45], loss tangent [32] and dielectric constant [32]. These changes may result from a discontinuous change in the activation volume at the glass transition to allow a smaller field value to bring about complete breakdown.

VI. Future Work

To extend the tests of the ESD models, additional time endurance tests will be conducted to improve statistics, to extend to lower fields and longer endurance times, and to test higher fields and shorter $t_{\text{en}}$ with more rapid ramp rates up the ASTM suggested maximum rate of 500 V/s. Future research will expand the temperature range of data in Fig. 10 below 120 K and above 300 K towards the polymer melting temperature. Additional tests will be conducted that cool to <150 K, apply a range of static voltages, and then measure current versus time data as the LDPE warms; these will study synergistic $T$ and $t_{\text{en}}$ effects and allow us to more fully understand the processes occurring around the glass transition temperature at $\sim 250$ K. Better statistics will also be acquired for the statistical analysis of recoverable breakdown events such as those shown in Figs. 6 and 9. Ultimately, different insulating polymers and ceramics (e.g., polyimide, PTFE, SiO$_2$, and Al$_2$O$_3$), with different defect density distributions will be studied.
Taken together, current and proposed measurements will allow us to conduct a comprehensive study of: (i) the stochastic nature of electrostatic breakdown; (ii) application of common statistical methods for used to describe ESD in materials [1,13] (iii) connections to the rate equations (Eqs. (6)), and (iv) a more complete development of the dual mechanism breakdown model of Eq. (10) outlined in this paper.

VII. CONCLUSION

This study of the breakdown of LDPE and polyimide for high applied fields in a capacitive configuration has produced a more complete picture of the time and temperature dependent breakdown behavior that suggests two separate processes are occurring, with their relative contributions to breakdown dependent on the value of applied field. As a result a new dual mechanism model for the probability of breakdown as a function of applied field, time and temperature, based on clearly identifiable physical parameters, has been developed to predict the ESD probability curves for applied field, endurance time, ramp rate, and temperature. This new model correctly predicts breakdown for a large range of applied fields, predicts the general behavior of the unusual transition observed from one process to the other, and yields material parameters from fits to the data that are consistent with previous studies of LDPE and polyimide. Results for the fits for several different measurements for LDPE and more limited polyimide measurements are listed in Table I.

The results of this study point out important consequences for spacecraft charging and other applications that build up charge or have sub-critical fields applied for long time periods. Measurements made with faster ramp rates over predict the breakdown field applicable for very slow charge accumulation by a factor of two or more. Further, the application of sub-critical fields by a factor of 2 or 3 less than the asymptotic breakdown field at short times still has endurance times far less than many typical long duration space missions. Taken together, these suggest that values of $F_{ESD}$ from standard handbooks, or cursory measurements that have been used routinely in the past, substantially overestimate the field required for breakdown in common spacecraft applications, which often apply sub-critical fields for very long time periods as charge accumulates.

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REFERENCES


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