

RESISTIVITY AS DYNAMIC BEHAVIOR IN LOW DENSITY POLYETHYLENE

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Abstract

Bridging the gap between theoretical calculations and experimental data has been the focus of much of the research into the electrical behavior of insulating polymers. Low density polyethylene is the standard test material used in both experimental work and numerical calculations. Resistivity measurements provide more than an absolute value for technical use; they also provide insight into the nature of active charge carriers and trapping behavior within LDPE.

Introduction

The industrial rate of formulation and use of polymers is increasing faster than the science and fundamental understanding of these complex materials. From the influence of physical processing on mechanical toughness to the long term affects of solvents added to the melt, the details of polymer history become significant when attempting to predict future behavior [1,2]. This dependence becomes particularly apparent in the determination of the electrical behavior in polymers. It should not be assumed, however, that no progress in characterizing these materials has been made. On the contrary, there is a wealth of theoretical and experimental work, as well as numerical calculations, which spans several decades of physical chemistry and polymer physics [3].

An appropriate beginning and perhaps the richest subject of study into the electrical properties of polymers is the examination of the resistivity of a given material [4]. Unlike metals or semi-conductors, much of the theoretical constructs are of extremely limited use in predicting resistivity behavior. Other avenues must be utilized to build the groundwork for explaining charge transport behavior in a polymer.

Furthermore, the resistivity itself proves to be a more complicated property in a polymer than semi-conductors, ceramic composites, or other simple dielectrics. LDPE has become the standard polymeric test material in determining electrical properties due to its relatively well characterized behavior and ubiquitous use.

The focus of this paper is to explore what information about the microscopic behavior of LDPE might be found in easily obtainable resistivity measurements.

Experimental Details

The measurements were carried out on chemically cleaned samples of LDPE that had been heated under vacuum to remove excess water that may have been absorbed during processing and handling. The presence of water or other surface contaminants can directly influence the surface states, which may extend deep into the band gap and create localized patches of internal electric field that contribute to degradation and sample breakdown [5].

Once inside the constant voltage chamber [6], the samples were maintained under a vacuum of 10^{-4} torr and subjected to an applied electric field

Applied Voltage (V)	Resistivity 1 ($\Omega \cdot \text{cm}$)	Resistivity 2 ($\Omega \cdot \text{cm}$)	Applied Voltage (V)	Resistivity ($\Omega \cdot \text{cm}$)
30	2.24×10^{18}	2.74×10^{18}	1100	2.51×10^{18}
70	2.65×10^{18}	3.97×10^{18}	1300	1.75×10^{18}
140	3.52×10^{18}	4.77×10^{18}	1500	1.65×10^{18}
200	4.00×10^{18}	4.65×10^{18}	1700	1.53×10^{18}
280	4.49×10^{18}	4.64×10^{18}	1900	1.28×10^{18}
340	5.11×10^{18}	4.24×10^{18}	2100	1.17×10^{18}
410	5.77×10^{18}	3.90×10^{18}	2300	1.06×10^{18}
480	6.86×10^{18}	3.49×10^{18}	2500	9.62×10^{17}
550	8.42×10^{18}	3.25×10^{18}	2700	6.17×10^{17}
620	1.04×10^{19}	3.12×10^{18}	2900	5.78×10^{17}
680	3.49×10^{18}	2.96×10^{18}	3100	4.84×10^{17}
760	5.00×10^{18}	2.95×10^{18}	3300	3.27×10^{17}
830	2.98×10^{18}	3.19×10^{18}	3500	2.89×10^{17}
900	2.97×10^{18}	3.63×10^{18}	3700	1.88×10^{17}
1000	3.05×10^{18}	3.39×10^{18}	3900	1.44×10^{17}
			4100	1.19×10^{17}
			4300	1.21×10^{17}
			4500	6.59×10^{16}

Table 1. Summary of measurement sets listing applied voltages and calculated resistivities.

for a period of one hour, followed by one hour with no applied electric field to allow the samples to discharge any accumulated charge. Leakage current through the material was measured using a Keithley 616 electrometer and the resistivity calculated for each of the applied fields. A summary of voltages and calculated resistivities is seen in Table 1. In the low field regime, two identical sets of measurements were taken. As shown in previous work, previous measurements affect the material in significant ways [1,6]. A graph of calculated resistivity at each applied electric field for both sets of measurements is shown in Fig 1a. Although the applied fields were identical, the resulting resistivities are very different. Once the second set of measurements concluded, we continued on into higher applied electric field regimes up to the point of electrostatic breakdown, the behavior of the resistivity becomes less unpredictable, shown in Fig 1b.

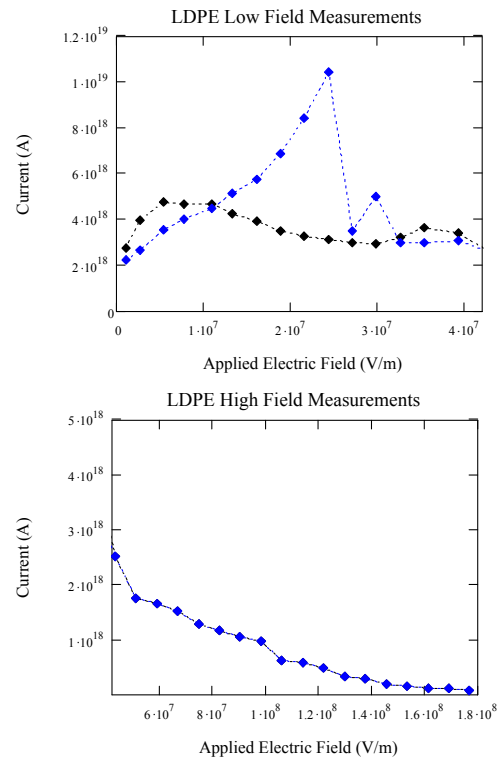


Fig. 1 a) Two sets of measurements were taken in the low field regime, b) one set was taken at increasingly higher applied fields until the sample suffered electrostatic breakdown.

In the high field data there are subtle differences seen in the calculated resistivities of sections of the data where the sample was allowed to sit, grounded, for a time period longer than one hour. Furthermore, a previous measurement for the purpose of determining electrostatic breakdown was taken on a virtually identical sample of LDPE and obtained an expected electrostatic breakdown of 6550 V at a voltage ramp rate of 50 V/s. The second sample broke down at 4500 V, significantly below the expected value. It has been shown that previous exposure to applied fields can dramatically influence the onset of electrostatic breakdown [7], resulting in the observance of electric field conditioning or charge memory within the samples themselves.

These measurements give a macroscopic picture of the dynamic resistivity behavior of LDPE. Closer examination of the resistivity data may also provide information about behavior on the microscopic level.

Internal Morphology

The typical chain structure of LDPE consists of $(CH_2)_n$ mer units in a planar zigzag configuration, see Fig. 2a. During quenching, where the polymer melt becomes a flexible solid, regions of semicrystalline material called lamellae form as the polymer chains fold back and forth parallel to each other [8]. A graphic depiction of these lamellae is shown in Fig 2b. Individual chains may fold several times, reentering the lamellae at multiple locations, or they can extend throughout several lamellae. Between the semicrystalline regions are areas of amorphous, lower density material. The chains with relatively high molecular mass crystallize preferentially,

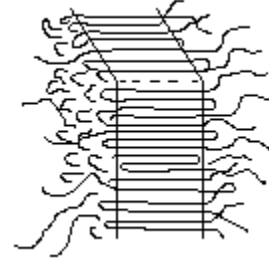
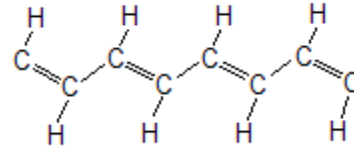


Fig.2 The lowest energy configuration of polyethylene chains is a) planar zigzag with alternating double bonds. During quenching, b) semicrystalline regions called lamellae form.

leaving the smaller chains and chain fragments to fill the interstitial areas [2, 7].

For long chain polymers, the degenerate molecular orbitals of the covalently bonded monomer molecules develop extended electronic states, allowing movement of charge carriers along the chain itself. However, in reality, these extended electronic states are interrupted by chain folds, pendant groups, residual reactant molecules, microvoids, or catalysts left behind by the manufacturing process [2,9]. The energy states are further localized by effects of polarization, internal electric fields, or relaxation, all of which contribute to segmental motion of the polymer chains. The areas of localized and extended states are marked by mobility edges [10,11]. Carrier mobility for LDPE can be calculated using Eq. 1, using $a = 0.254$ nm as an estimated lattice spacing [9] for the lamellae regions,

$$\mu_{\min} = \frac{2\pi ea^2}{8h} \quad (1)$$

with a value of $\mu_{\min}=1.2 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, this calculation does not account for the difficulty in carrier movement from chain to chain and experimental measurements of mobility are typically orders of magnitude lower than this calculation [2,9]. Necessarily, this mobility, μ_{\min} , then applies only to interchain conduction.

During interchain conduction, excess electrons are driven along the chain backbone, repelled by Pauli exclusion [9,15], and tend to preferentially gather in the interspatial regions of lower density. Mobile electrons push against the surroundings chains to create lower density, and lower energy, areas as they move along the chains [15]. These fluctuations of lower density areas, particularly under the influence of mechanical or electromagnetic forces, result in areas of the material that increase and decrease in size. At the nanometer scale, these changing spaces create thermal density fluctuations that can be observed as electrical noise [8,11,12]. A closer look at the resistivity measurements in the low field regime reveal a level of electrical noise in the current measurements that is much greater than the electronic noise of the experimental system itself. See Fig. 3. The interstitial spaces of lower density that serve as collector sites for mobile charge carriers increase in size under an increasing applied electric field [8]. Detailed calculations of electrical noise due to thermal density fluctuations are far beyond the scope of this paper.

As the applied field increases, an increase in sudden internal discharges is observed. See Fig. 4. These localized patches of internal electric fields contribute strongly to the onset of dielectric breakdown [7,14]. It is theorized that as the applied field

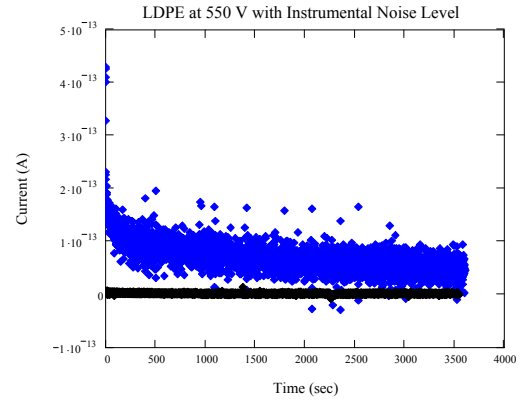


Fig. 3 At 550 V, the characteristic leakage current measured through LDPE is significantly noisier than the noise of the system and in comparison to the currents obtained from materials with lower resistivities.

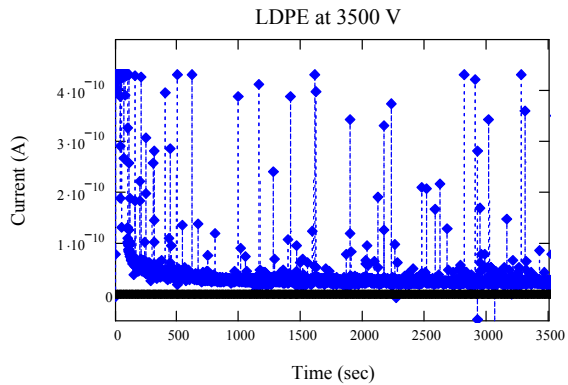


Fig. 4 At 3500 V, there are a significant number of internal discharges seen in the LDPE sample, where localized internal electric fields build up and discharge, contributing to the onset of dielectric breakdown.

increases, the traps in the interstitial area are less and less efficient and the mobile electrons begin to gain enough energy for intrachain conduction and are expelled from the material, resulting in the measured leakage current used in resistivity calculations [13]. Increasing fields allow for larger pockets of localized fields to develop within the amorphous interstitial areas. The electrical noise caused by thermal density fluctuations appears to decrease, but the causes and mechanisms behind

these behaviors remains highly controversial [3,10,15].

Conclusions

Accurate measurements of the resistivity of LDPE are extremely valuable for use in material design and anticipating material properties. Since LDPE has become an integral part of technology, from electrical cable insulation found in a typical household to numerous components of aircraft and spacecraft, it is vital that its electrical behavior is well characterized and understood. The macroscopic resistivity behavior has been found to be dynamic and sensitive both to the manufacturing process and the history of the sample, a property which requires great care during experimental measurements.

A deeper look into resistivity measurements gives tantalizing hints into the behavior at the microscopic scale, where the molecular properties become increasingly more important. Much more work remains to be done to determine the mechanisms of charge transport through LDPE and other insulating polymers.

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