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Electric Field Induced Hopping Conductivity and Polarization in Hytrel

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4900 Project
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April 20, 2007

Introduction

The focus of my 4900 research project is centered on the conductivity of Hytrel, a complex, newly-developed block co-polymer. I first began to study Hytrel during the summer of 2006, as part of the USU College of Science Mini-Grant program¹. My general objective was to study the relationship between the resistivity of Hytrel and hopping conductivity. Hopping conductivity is a theory of electron transport for non-conducting solids, originally developed for amorphous semiconductors^{2,3}. The theory will be examined in greater detail later in this document. While studying this relationship last summer, I noticed an unusual phenomenon in the Hytrel data. When subjected to an electric field, Hytrel responds very slowly. The initial response of thin-film dielectrics to an electric field is typically understood to be governed by the polarization of the polymeric chains. What I seemed to be an unusual polarization in Hytrel formed the impetus for my project.

Hopping Conductivity

As stated before, hopping conductivity is an electron transport model for non-conducting solids. Although I will not go into the intricate theoretical details, hopping is essentially the quantum mechanical tunneling of electrons between localized states or traps in a given material⁴. The ability or likelihood of an electron tunneling from one localized state to another is governed by well depth, Δh , and well separation, a (See Fig. 1).

In the depiction to the right, traps are depicted as potential wells. Hopping is favored in a direction determined by an external electric field. Although this is much simplified version of reality, it serves to illustrate many of the important parameters that influence hopping probability.

A relatively simple equation for the probability of hopping is

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

Of especial note in this equation are four parameters. First, we see the Δh and a , which have already been discussed. Also note that this equation assumes a single value for each. This will come into play later. Also, we have two experimentally controlled parameters, the electric field E , and temperature T which influence the probability of hopping.

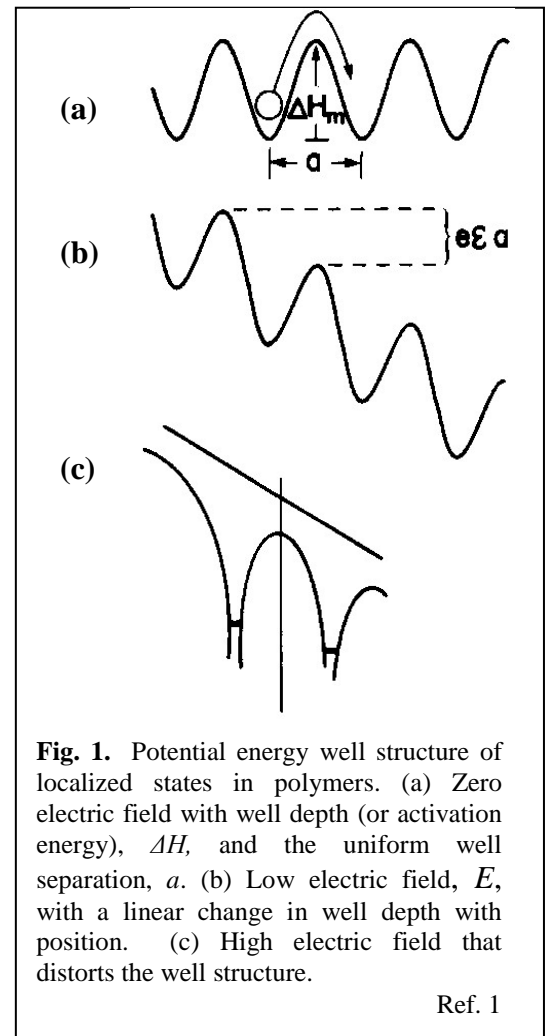
The theory of hopping conductivity was originally developed, and since verified, for amorphous semiconductors.

Although some may argue that it is also appropriate for complex polymers, its degree of applicability in such instances is questionable⁵. It is understood that the inherently high order of disorder in polymeric structure is expected to lead to localized states.

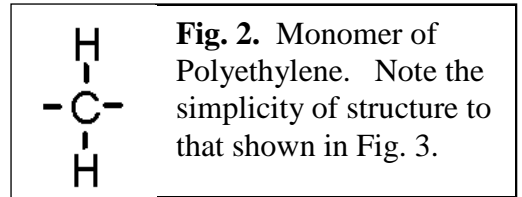
These localized states can then act as trapping sites, thus enabling hopping conductivity. Unfortunately, very little experimental evidence exists to decisively establish the degree of applicability of hopping conductivity models to polymers.

Hytrel

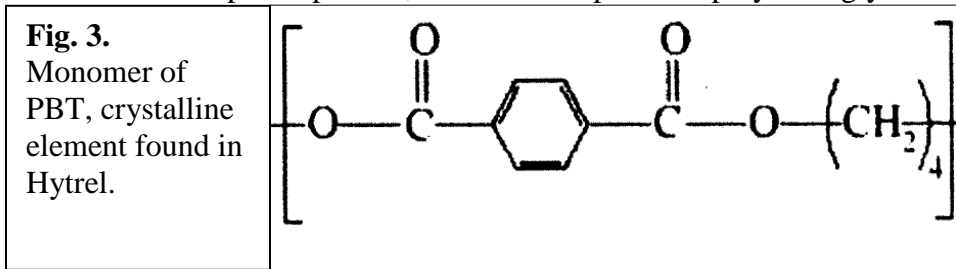
While one may wish to avoid naively diving into the chemists' realm, a closer look at Hytrel's complex molecular structure will yield some valuable insights. To begin with polymers in general, a polymer is a chain of several units. Each of these units is known as a monomer (Fig. 2). One common, relatively simple polymer



is polyethylene. A molecule of polyethylene is typically a polymeric chain of hundreds of monomers. Although each monomer is not itself overly complicated, the situation gets worse when we consider a solid composed of these polymeric chains. Their orientation is often modeled by what is called a self-avoiding random walk². This is similar to a three dimensional Brownian motion, limited by the stipulation that the chain can not go where it has already been. On a macroscopic scale, behavior is not always predictable. Microscopically, the chains are coiled and twisted into a complex configuration often compared to spaghetti. There can be no conversation of any long range order.



Hytrel is complex, even for a polymer. The complexity of the molecular structure far exceeds that found in simpler polymers, such as polyethylene. Because Hytrel is newly developed, many details of its molecular composition are not known. What we do know, is that it is a block co-polymer, meaning it is a combination of different polymeric elements. There is a crystalline portion, which has been identified as polybutylene-terephthalate or PBT (see Fig. 3). There is also an amorphous portion, which is composed of polyether glycols. The relative concentration of each component and the precise molecular composition of the glycols remain as of yet unknown.



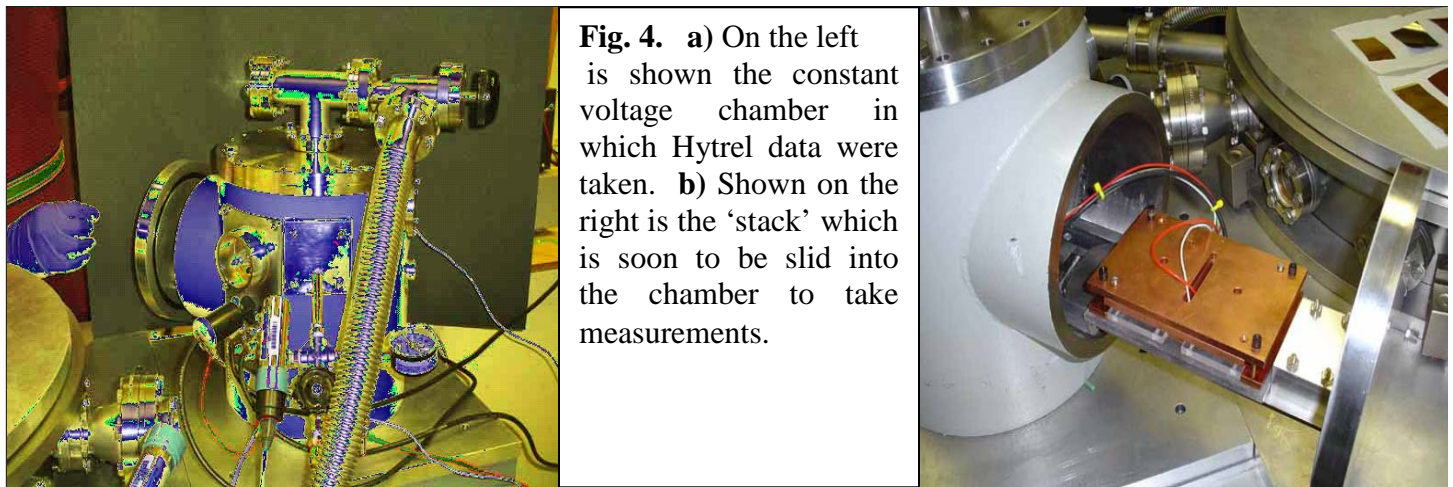
It is expected that the high degree of complexity of Hytrel's molecular structure should increase the distribution of localized states.

Or in other words, the distributions of 'Δh' and 'a' will increase. This increased distribution of states contributes to an effect that will be discussed shortly.

Sample Preparation and Experimental Method

The Hytrel samples were prepared by first cleaning them with methanol, and then vacuum baking them in order to remove excess water molecules that could skew our results. After baking, the samples are placed in a nitrogen filled storage compartment until measurements are to be taken.

The measurements take place in the constant voltage chamber (see Fig. 4a), a vacuum chamber which achieves pressures of 10⁻⁴ Torr or less. The thin film sample is mounted on an aluminum high voltage plate, and sandwiched on the opposing side by an electrode. The sample thickness is 9 mils. The 'stack' consisting of the plate, sample, and electrode is then slid into the chamber (see Fig. 4b).



An electric field is applied across the sample, which results in some current flow through the sample. This current is measured with a high-precision electrometer. By employing shielding and other techniques, the system has been refined to the point that instrumental resolution of the electrometer is the primary current measuring limitation. The noise level is thus held at or below 2.0 x 10⁻¹⁵ amps. Hytrel typically allows current

flow of 3-4 orders of magnitude greater than this, so that electrical noise is not a problem. To examine Hytrel's response to various magnitudes of electric field, I used an applied voltage anywhere from 10 V up to 2000 V. Due to Hytrel's very slow response, a single run could last longer than 24 hours. In the interest of time, I concentrated my efforts on low electric field measurements (<10% ESB). Data was taken at $\Delta t = 1 \text{ sec}-10 \text{ sec}$. Due to the long time scale of measurements, this allowed nearly 5 orders of magnitude of time to be spanned.

Measurements

Figure 5a shows a fairly typical example of a data set. Initial current is high, and then slowly approaches an asymptotic limit, determined by the resistivity of the sample. Figure 5b is a graph of the same data, only this time portrayed on a log-log plot. The unique shape is striking. There is initially a decrease which lasts for about 2 minutes. Then there is a distinct bend in the curve, after which the decrease is heightened.

To make matters even more interesting, several runs at various low electric field strengths are plotted on a single graph (see Fig. 6), each run showing the bend. It is entirely reasonable to propose that the initial portion of each curve can be modeled by a power law. Furthermore, the slopes of the first power law for each run are identical, as are the slopes of the second power law for each run. Both the shape of the linear plot and the power law dependence of the log-log plots suggest a possible relation to dispersive transport.

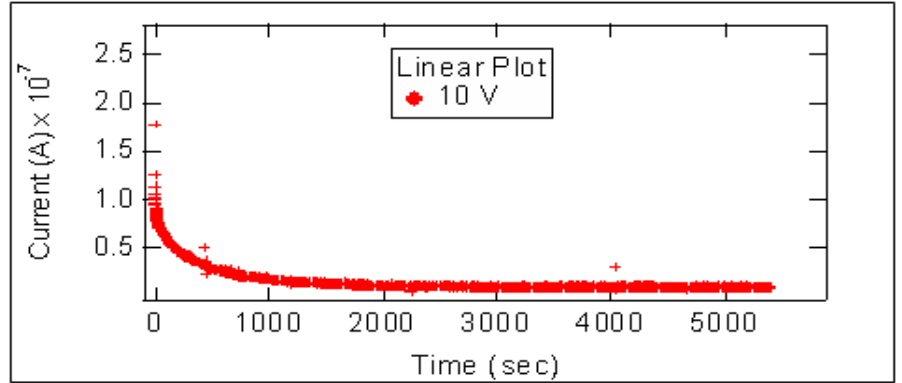


Fig. 5. a) Above is a graph of current vs. time resulting from a 10 V potential. b) Below is the same graph, viewed on a log-log plot. Note that at around $t=120$, there is a bend in the curve.

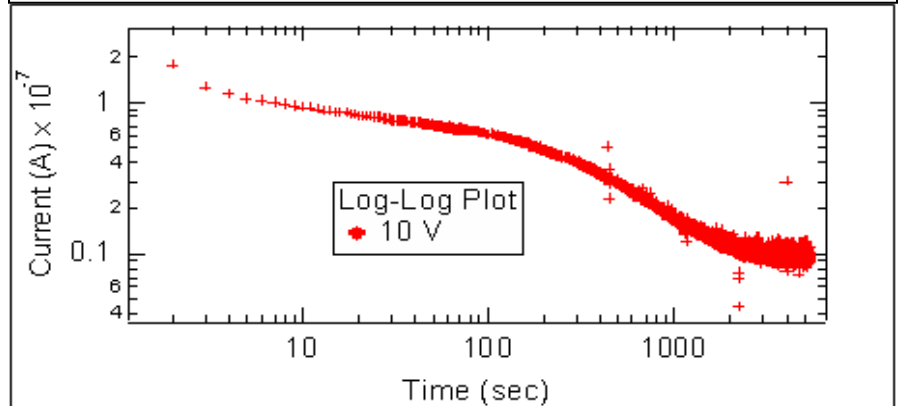
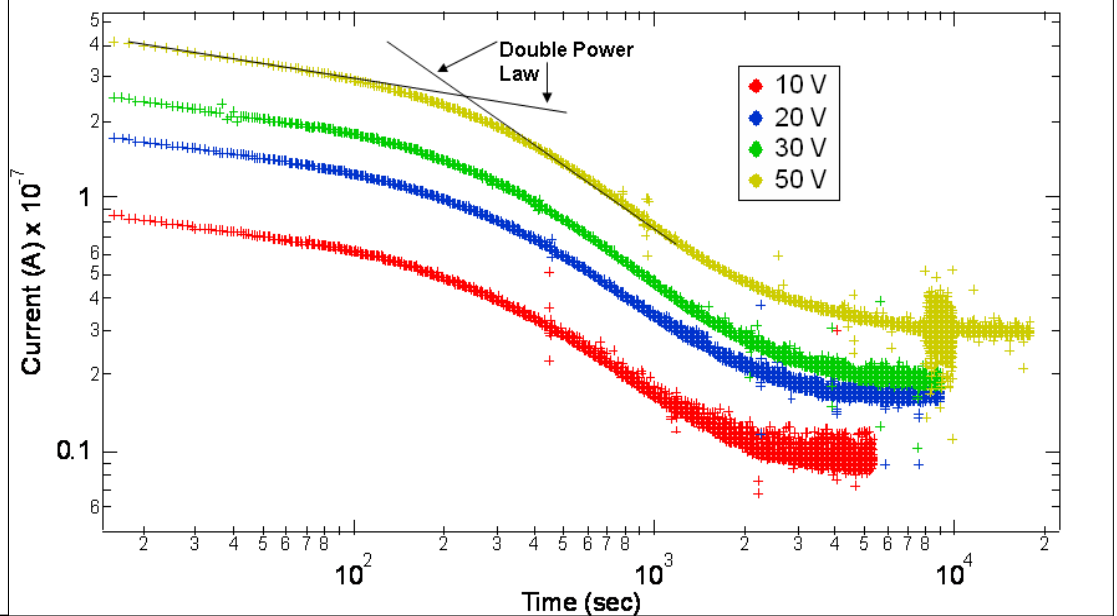


Fig. 6. Plotted are 4 different runs at various low electric fields. When plotted as shown on a log-log graph, the characteristic bend is seen in each of the graphs.

The slope before the bend is identical for each run, as is the slope after the bend for each run. The initial portion of each run can thus be modeled by two power laws.



Dispersive Transport

Consider first a thin film of material in which normal transport occurs. As the result of some form of brief excitation, electrons began to transport through the material. As time elapses, the charge ‘packet’ spreads in accordance with diffusive laws, but it remains a) a distinct pulse and b) Gaussian in shape. (See Fig. 7, 8) A plot of current vs. time in such case is very step-like. In hopping conductivity theory, such transport is expected to result from single values for ‘ Δh ’ and ‘ a ’⁶. Now consider non-Gaussian, or dispersive transport. Dispersion now occurs to a much greater degree. In fact, although the charge centroid moves through the material, the peak of the pulse does not. Thus, dispersion is the primary cause of current. The corresponding plot of current vs. time is initially high and has a long low tail (Fig. 7, 8). In hopping conductivity theory, this behavior is expected to result from a large distribution of Δh and a . (Remember that such a distribution is expected also to result from Hytrell’s complex molecular structure.)

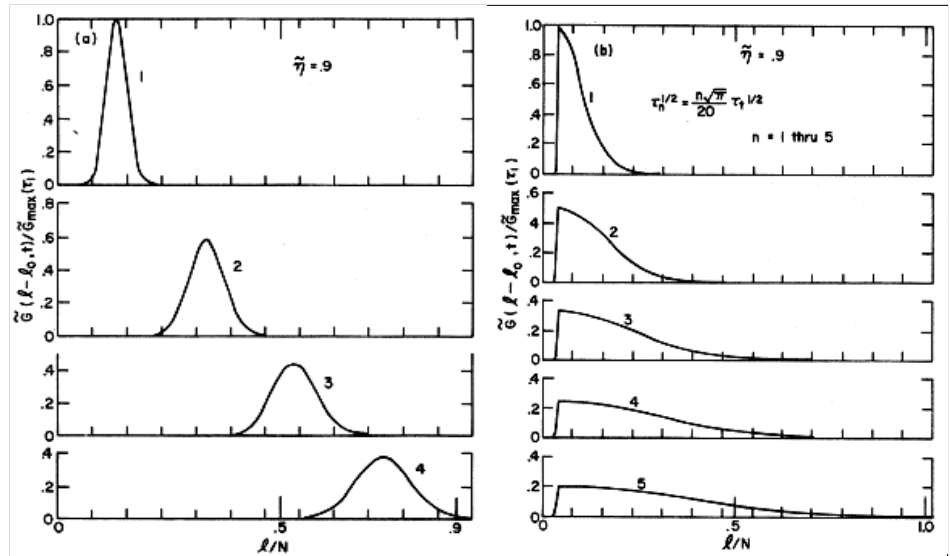


Fig.7. On the left is depicted a pulse characterized by normal transport. Although dispersion occurs to a small degree, the pulse is still a coherent pulse and Gaussian in shape. On the right is depicted a pulse characterized by dispersive transport. The electrons do not stay in a pulse, but always have a maximum near the beginning surface. Dispersion is responsible for charge transport.

Both Fig. 7 & 8 adapted from Scher and Montroll (see Ref. 6)

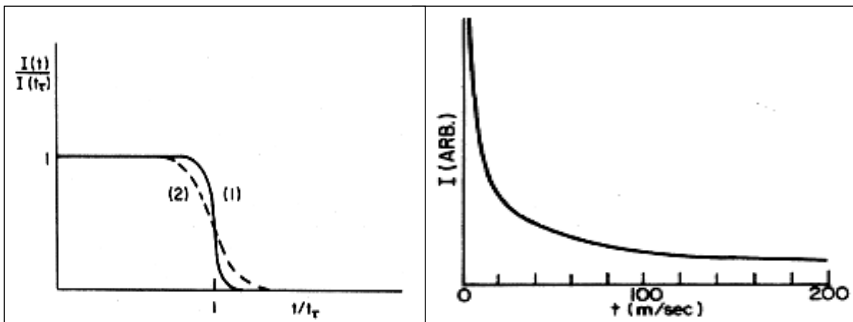


Fig. 8. On the far left is the step-like graph of current vs. time resulting from normal transport. To the immediate left is the characteristic shape resulting from dispersive transport. Note the initial high value in current, followed by the asymptotic tail.

Dispersive Transport in Amorphous Semiconductors

A great deal of pioneering work on dispersive transport was done in the 1970’s by G. Pfister, Harvey Scher, and Elliott W. Montroll.(ref.) First Scher and Montroll in a 1975 paper describe the phenomenon. In a 1978 paper Pfister and Scher treat it more extensively. While much of the theoretical development is beyond the scope of this document, some of their conclusions are of particular interest.

Figure 8 shows a graph from the 1978 paper of Pfister and Scher⁷. To produce this graph, they performed photoconductivity experiments on amorphous selenium, a disordered semiconductor. The experiments were performed by placing a thin sample between insulated electrodes, used to produce an electric field, but not provide direct electrical contact to the sample. A short burst of light then excites electrons on one edge of the sample. Current is measured as the electrons are transported across the sample under the influence of the electric field. When viewed on a log-log plot (as in Fig. 8.), the current is seen to be governed by two power laws, which is reminiscent of what was seen in the Hytrell data. This unique shape viewed in a log-log plot is shown by the authors to have been caused by dispersive transport. In normal transport, a transit time is simple to define. In dispersive transport, the bend in the curve is chosen as the transit time (t_T).

Because this data was obtained for an amorphous semiconductor, and because hopping conductivity models are viable for semiconductors, the authors attributed this electron transport phenomenon to hopping. A broad distribution in hopping event time is assumed. (A broad distribution in hopping event time would most readily be caused by a broad distribution of Δh

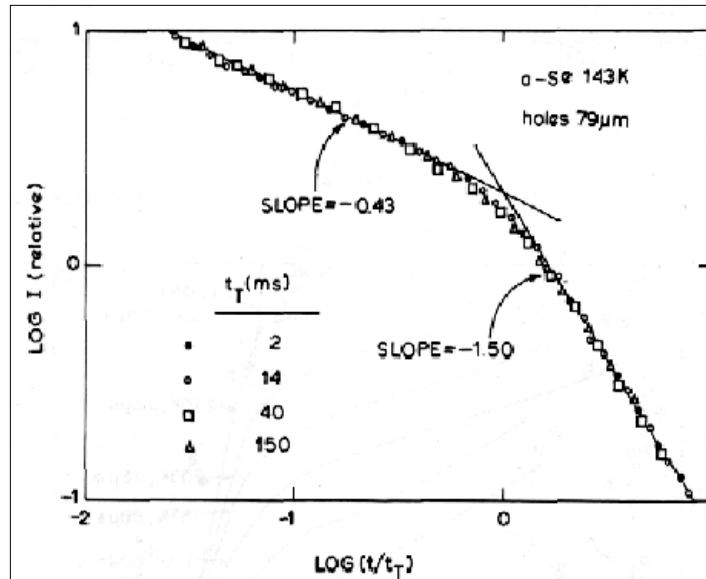


Fig. 9. This graph shows data obtained from photoconductivity experiments performed on amorphous selenium. A double power law dependency of current on time is evident. Data is superimposed from several data runs. This ‘universality’ graph is a clear indicator of dispersive transport.

and α .) This distribution can be approximated as $\Psi(t) \sim t^{-(1+\alpha)}$, where α is a constant between 0 and 1. From this relation, the authors derived an expression for current before and after t_T . Thus we have the algebraic relations $I(t) \sim t^{-(1-\alpha)}$ for $t < t_T$, and $I(t) \sim t^{-(1+\alpha)}$ for $t > t_T$. It is of interest to note that the exponents sum to -2. Also we notice that the sums of the power law slopes viewed in the graph indeed sum to approximately -2.

Another interesting aspect of the graph shown in Fig. 8 is that the curve is of several data runs at various electric field strengths, superimposed by normalizing both axes in respect to t_T . The ability to thus superimpose data is called ‘universality.’ The authors argue that universality is direct evidence of dispersive transport.

Universality of Hytrel

Because the Hytrel data exhibited behavior suggestive of dispersive transport, I attempted to show its universality by producing a graph similar to that shown in Fig. 9. The result is Fig. 10. The universality of the Hytrel data is demonstrated here without ambiguity. The universality, in turn, demonstrates the exhibition of dispersive transport in Hytrel.

Before one ought to begin to make conclusions, a key dissimilarity must be observed. The photoconductivity experiments employed a short burst of light to excite electrons. For Hytrel, the sample was in direct contact with the plate, meaning it was constantly being ‘fed’ new electrons. This disparity in experimental method is judged significant and is under current consideration.

We do not, however, consider this reason to doubt the dispersive transport we see clearly manifested in Hytrel. Another oddity is that the slopes add up to -1, not -2 as in Fig. 9. It is possible that this difference is a result of the experimental method. It is also possible that the algebraic distribution function used to approximate the current for amorphous semiconductors is not wholly applicable to the insulating material, Hytrel, but rather that some other distribution function must be used. This possibility is also currently under consideration.

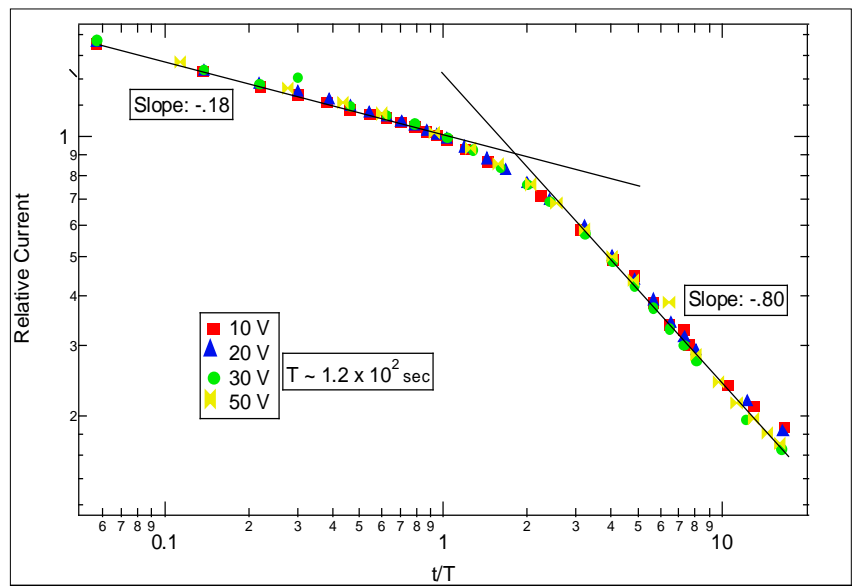


Fig. 10. This graph shows the definite universality of Hytrel. Data from 4 runs at low electric field strengths are superimposed onto a single curve. This universality curve is considered direct evidence of dispersive transport mechanisms operative in Hytrel.

Finally I must mention a very remarkable comparison: The transit time found for amorphous selenium is on the order of milliseconds, while that for Hytrel is on the order of 100's of seconds. That dispersive transport is also observed in Hytrel, albeit at a time scale difference of 5 orders of magnitude, is very striking.

Future Work

The avenues of future work relating to Hytrel and dispersive transport are numerous. Fig. 11 shows the same data as Fig. 6, with three runs at higher electric field appended. It seems to appear that a transition from a double power law to a single power law is occurring. Such presumptions are as of yet, unfounded. Data is needed to extend the time frame; also, even higher electric fields need to be applied and the resulting data examined. As discussed in the preceding section, the effect that the experimental method has on dispersive transport needs to be thoroughly examined. Also, if applicable, a hopping event time distribution function for Hytrel needs to be derived. Dispersive transport in amorphous semiconductors exhibits a sample-thickness dependent transit time. This could be studied in Hytrel. And finally, hopping probability is heavily dependent on temperature, making constant temperature measurements over a wide range of temperatures a priority.

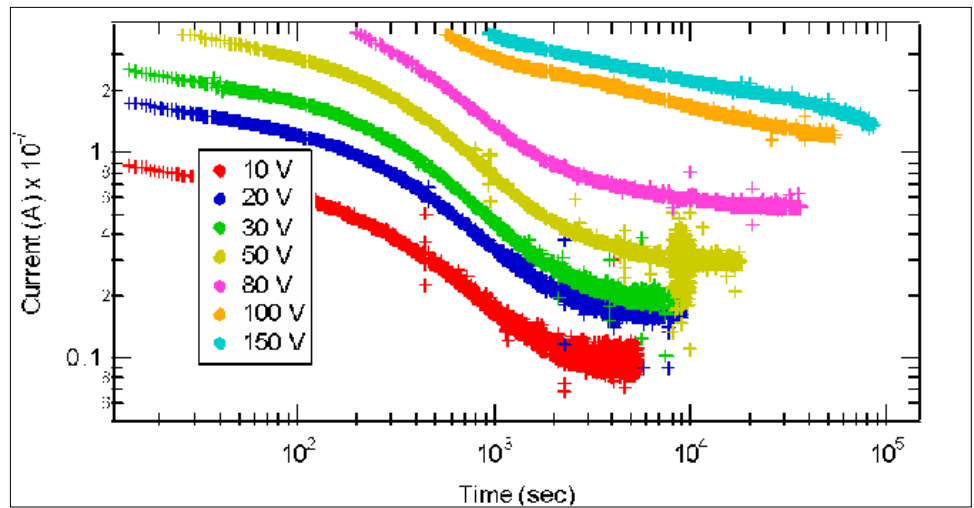


Fig. 11. A more comprehensive data set than shown in Fig. 6. It seems that a possible transition from double-power law dependence to single-power law dependence may be occurring.

Conclusions

- I have taken a good, though partial, data set of Hytrel's conductivity at a constant electric field over a wide time range.
- Hytrel has been found to exhibit markedly different behavior than that exhibited by simpler insulating polymers and the difference in behavior can likely be attributed to the molecular complexity of Hytrel.
- It has been shown that the low-electric field Hytrel data are in good qualitative agreement with dispersive transport models developed for amorphous semiconductors - even at a time scale difference of 5 orders of magnitude.
- Although no thorough description of the applicability of hopping conductivity models has been given, a link between the conductivity of Hytrel and the conductivity of amorphous semiconductors has been established.

Acknowledgements

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