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Ion mobility time of flight measurements: effect of experimental parameters on measurements in a non-hydrogen bonded system

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Abstract

An in situ measurement technique that isolates the mobility of charge carriers is described and analyzed. The technique allows significant improvement over conductivity measurements to monitor changes in the physical properties and state of a material as it cures. This is essential in systems where N_i, the number of charge carriers, cannot be assumed constant such as during cure of epoxies, urethanes and polyimides. Currently, there is an assumption made in the literature that the number of charge carriers present in a curing material is constant when conductivity is used as an in situ measurement technique to monitor changes in mobility (and thereby viscosity). This assumption is widely used, for example when dielectric conductivity measurements are correlated with changes in properties such as viscosity. Ion mobility, time of flight (ITOF) measurements, which are described here, are an appropriate technique to isolate and measure particle mobility due to changes in the state of the material. Furthermore, the ITOF technique, coupled with the measurement of σ, the dielectric conductivity, allows one to measure *separately* changes in the mobility and the number of charge carriers due to curing or changes in temperature. This is possible since conductivity is the product of the number of charge carriers and their mobility. Length of pulse, strength of applied field, sensor geometry, and temperature/viscosity are examined to determine optimum parameters of measurement for a simple, non-curing system: dimethacrylate of tetraethoxylated bisphenol A (D121). This paper seeks to show that with changes in viscosity, the pulse length and magnitude of voltage in relation to the distance between the electrodes should be varied to obtain accurate ITOF information on the changing mobility.

Keywords: Ionic mobility; Dielectric cure monitoring

1. Introduction

The ability to characterize and monitor in situ the advancement of a polymerization process, and the corresponding changes in processing properties in a non-destructive way has been developed. However, there are still many relationships to be fully understood. In particular, knowledge regarding the relationship of viscosity to changes in electrical and material properties throughout the reaction is highly desired [1–29].

Typically the electrical conductivity, σ, is obtained through dielectric measurements using an in situ micro-sensor and a multi-frequency impedance analyzer. The impedance of a material is measured over a range of frequencies, allowing the determination of capacitance (C) and conductance (G). The measured complex impedance Z^* value is related to C and G by:

$$\frac{1}{Z^*} = G + i\omega C \tag{1}$$

where $\omega = 2\pi f$, and C and G are geometry dependent. Knowing the value for C_o, the air replaceable capacitance of a sensor with a known geometry, the geometry independent complex permittivity, ε^*, of a material can be determined. The quantity ε^* is the difference of ε' and $i\varepsilon''$, which represent the real component of dielectric permittivity and the imaginary component (i) and loss, respectively.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{2}$$

Where

$$\varepsilon' = \frac{C_{\text{material}}}{C_o} \tag{3}$$

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and

$$\varepsilon'' = \frac{G_{\text{material}}}{C_o \omega} \tag{4}$$

In general, at low viscosities, low frequencies, and high temperatures, the ionic conductivity dominates the impedance of a material. In this case [1],

$$\sigma = \varepsilon_o \omega \varepsilon'', \tag{5}$$

Where ε_o is the relative permittivity of free space (8.854×10^{-12} F/m). The ionic conductivity of a polymerizing material on a molecular level is a sum of the product of the number of ions present and their respective mobility [2].

$$\sigma = \sum N_i \mu \tag{6}$$

where μ is the mean mobility of the ion, and N_i is the mobile ion concentration of that species. The relationship between viscosity, a macroscopic characteristic, and ionic conductivity, on the molecular level, has been studied in detail [1–29]. These studies have focused on relating σ and using in situ measurements of σ during cure to monitor viscosity as well as other critical cure processing properties such as reaction advancement and buildup of the glass transition temperature, T_g. Typically, when discussing σ, the contribution of the number of charge carriers is neglected or assumed constant, and σ is assumed to track μ (mobility). For an approximate understanding of the ion's translational mobility in a curing system, measurement of σ provides a good estimation. However, the method of using σ to measure mobility is questionable for systems where the number of charge carriers, N_i, is not a fixed value as in epoxies, polyimides, and polyamides. Here the number of available proton donating groups changes with the advancement of the reaction. In these hydrogen-bonded systems, proton conduction and free ions can result in a variable number of charge carriers. Here the approach of conductivity relating directly to viscosity is based on a constant ionic concentration and must be evaluated, as it is a questionable approximation. When the number of charge carriers varies in addition to changes in their mobilities, the fundamental relationship between viscosity and conductivity based exclusively on changes in mobility is no longer valid.

A combination of measurement techniques that isolates both the number of charge carriers and their mobility allows significant improvement in monitoring changes in the state and structure of a material as it cures and is essential in systems where N_i cannot be assumed constant. Ion time-of-flight measurements are an appropriate technique to isolate and measure particle mobility due to changes in the state of the material. The time-of-flight technique, coupled with the dielectric measurement of σ, allows one to determine separately changes in the number of charge carriers, along with changes in mobility of a polymer due to cure or temperature.

This paper describes the measurement parameters needed to obtain accurate ion mobility, time of flight (ITOF) data over a wide range of temperatures, viscosities, length of voltage pulses, and magnitude of the applied fields. In earlier papers, the ITOF technique has been used at a fixed voltage and pulse length and was shown to confirm dielectric experiments [30–33]. In these reports the material experiences significant changes in viscosity as the polymer reaction advances.

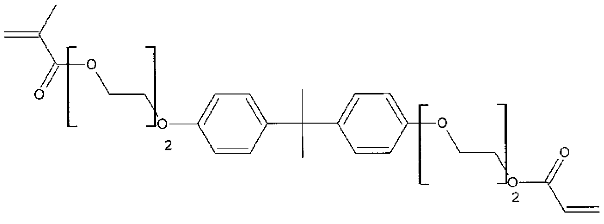
The work described here suggests that the past approach of using a fixed set of pulse lengths and applied voltages during polymerization when the viscosity is increasing over many decades in magnitude is subject to question. This paper seeks to show that with changes in viscosity, the pulse length and magnitude of voltage should be varied to obtain accurate ITOF measurements of mobility and that the pulse length and voltage need to be tailored to the distance between the electrodes. Without understanding these relationships, ITOF cannot be applied properly.

2. Materials

In order to isolate the effect of the pulse length and voltage on measurements of mobility in a system where only the viscosity is changing, a non-reacting system without hydrogen bonding was chosen and the temperature was varied. This results in controlled changes in viscosity with no change in the number or type of mobile ions. A simple non-hydrogen-bonded system, dimethacrylate of tetraethoxylated bisphenol A was the primary material investigated. It is commercially known as a dimethacrylate monomer D121 (Fig. 1). It experiences a large change in viscosity over a convenient range of temperatures with no degradation.

2.1. Equipment

A current/voltage source-measurement unit, Keithley 237, was used to control the voltage and measure the output current flow. Data was stored with an IBM/PS2 computer and collected with software developed specifically for this application. Current measurements were taken every 0.33 s and plotted versus time in seconds. The temperature was controlled by a Thermolyne 47900 Furnace above ambient,



D121

Fig. 1.

and by a Delta Design 9015 forced air oven for below ambient. A Barnart thermocouple monitored the temperature of the sample during the time of the measurements (Fig. 2).

Two commercial products were chosen as in situ sensors. An idex sensor (036S), purchased from Micromet, Inc., consisted of nickel electrodes on a 14″ flexible polyimide substrate, with an air gap of 115 μ. A small air capacitor (160-110-1), purchased from Cardwell Condenser Corp., had a large beryllium copper compression rotor contact, and nickel-plated-steatite ($Mg_3Si_4O_{10}(OH)_2$) metal parallel plates, which had a 430 μ air gap. Both of these geometries produced no measurable current when tested alone in air, and were able to provide good measurements of the ion mobility as monitored by times of flight.

Dielectric measurements of conductivity were made using a Hewlett Packard (HP) model 1492A Impedance Analyzer and a TA Instruments model 2970 Dielectric Analyzer.

2.2. Measurements of ion mobility time of flight

Time-of-flight is a measure of the length of time an ion takes to travel across a fixed distance between two electrodes with a given potential. Starting from an equilibrium ion distribution (a), the electrodes are oppositely charged (b), and the attraction of unlike charges causes the anions to move towards the positively charged plate, while the cations migrate to the negative plate (c) (Fig. 3).

The Keithley source applies a square-wave voltage pulse to the system for a fixed length of time (Fig. 4).

At a particular time after the initial pulse, a peak is observed in the measured current, $I(t)$, in each subsequent pulse. This peak represents the point in time when the highest rate of ions is arriving at the electrode, resulting in a peak in the measured current, I [30–32].

Simply reversing the charges on the plates creates the pulse sequence, and the ions are then drawn to the opposite plate. Here (Fig. 5) the measurement pulse sequence involved four sets of equal length pulses. The time-of-flight flight time occurs at the peak in the output current versus time after a reversal of voltage polarity. This time marks the time of maximum number of mobiles species arriving at the electrodes and characterizes the ion transit time. These measurements are repeated while conditions within the experiment are changing. The ITOF is dependent on these changing variables including: changes in the viscosity of the medium due to a change in temperature or a chemical reaction, the measurement parameters such as the fixed distance between electrodes (sensor material and geometry), the possibility of a charge polarization effect on the plates after a given time, the length of time allowed before the pulse is switched, and the magnitude of the applied voltage.

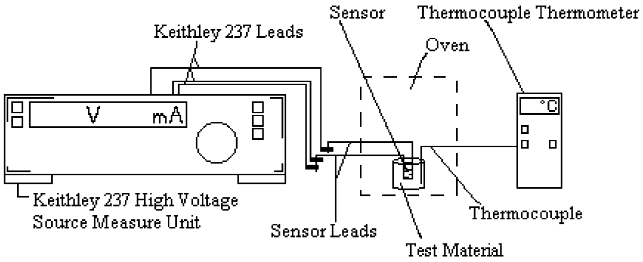


Fig. 2.

The effect of these variables on the ITOF measurements can be described mathematically. The ionic mobility, μ, is defined as the ratio of the velocity, v, and the magnitude of the electric field, E

$$\mu = v/E \tag{7}$$

neglecting internal field effects, the electric field acting on the ions is:

$$E = V/d \tag{8}$$

where V is the applied voltage, and d is the distance between plates. We can substitute (Eq. (7)) into (Eq. (8)) to yield

$$v = \mu(V/d)$$

substitution of $v = d/t$ gives

$$\mu(V/d) = d/t \tag{9}$$

rearranging to solve for t gives us an expression for the ITOF.

$$t = d^2/\mu V = \mathrm{ITOF} \tag{10}$$

From this equation, we can see that ITOF is dependent on the distance between the electrodes in the sensor, the mobility, and the applied voltage. Since mobility is observed experimentally to be inversely proportional to viscosity to a power a, where $a \leq 1$, we can rewrite the above equation as

$$\mathrm{ITOF} = K\eta^a/V \tag{11}$$

where K is a constant.

2.3. Rheology

The viscosity of D121 was measured using a TA instrument AR 1000 rheometer over the temperature range of −15–100 °C. Aluminum parallel plates were used in oscillatory measurements, each plate with a diameter of 40 mm, housed inside an environmental test chamber. Measurements over an ambient temperature range were also taken with Peltier Plate geometry. Experiments were performed in a temperature ramp, controlled stress mode, and cycled through a range of frequencies from 0.1 Hz to 1 kHz.

2.4. Dielectric impedance measurements

Two measurement systems were used to measure the

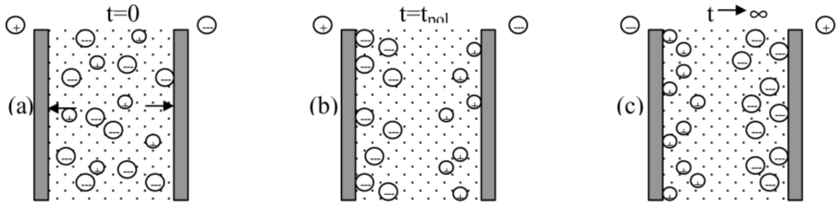


Fig. 3.

dielectric conductivity of the system. The TA dielectrometer using a single interdigitated sensor was used to measure the responses to a frequency sweep. The conductivity was determined from the frequency dependent values of ε'', where values of $\varepsilon''*\omega$ were independent of the frequency. The HP impedance analyzer was also used, coupled with an interdigitated quartz sensor, to measure the conductance and subsequent capacitance of the material over a range of temperatures and frequencies.

3. Results and discussion

3.1. Polarization effects

First, the pulse length together with magnitude of applied voltage was examined. Pulse length dependent data is analyzed at a fixed temperature of 40 °C, and is reported in Figs. 5 and 6. Other temperatures show the same results. An inter-digitated (idex) sensor system (Fig. 6) and a parallel plate, air capacitor system (Fig. 7) were used to acquire the data.

To see the effect of varying pulse length coupled with the magnitude of the applied voltage at 40 °C, as well as other temperatures, the log of ITOF $*$ V versus the pulse length for each type sensor was plotted for a series of voltages. Because ITOF $= d^2/\mu V$ (Eq. (10)), the product of ITOF and voltage is the quantity which monitors the ion mobility, μ, for a fixed distance d between the plates of the measurement capacitor. If the experimental material has a fixed number of ions, the mobility is unchanging, and at a fixed temperature and constant viscosity, the product of ITOF and voltage will return a constant value.

The plots for both sensor systems (idex and small capacitor) show that all the values of ITOF $*$ V do not all fall at a single value, as indicated by Eq. (10) as the voltage and pulse length change. Rather there is a range of pulse lengths and voltages where Eq. (10) is valid. That is, ITOF $*$ V is a constant for a range of pulse lengths and voltages, but not for all pulse lengths and voltages. As the voltage and pulse length become either smaller or larger than the optimum range the values of the product of ITOF $*$ V are no longer constant. There are two major reasons for this deviation from Eq. (10). If the pulse length is too small and/or the voltage is too weak, ions migrate only partially to the opposite plate. That is, the major concentration of charge is between the two plates and not at the electrode surfaces. When the voltage is reversed on the electrodes, the shorter distance for the major concentration of ions to travel produces a smaller value for the ITOF. On the other hand, if the voltage is too strong, and/or the pulse length is too long, a polarizing and discharging process at the electrode can be created [34–36]. When the voltage is reversed on the electrodes, an additional time is needed to reverse this excess effect at the electrodes and pull the ions from plates. As a result, one observes a longer than expected ITOF.

For Fig. 6 with an idex sensor, the value of ITOF $*$ V where Eq. (10) is obeyed is indicated by the lines outlining those experimental values where the ITOF $*$ V is a constant for those voltages and pulse lengths. The correct value of log(ITOF $*$ V) for this line is approximately 2.0 and is indicated on the axis by a box.

In the case of the air capacitor, a similar range of pulse lengths and voltages corresponding to a fixed value of ITOF $*$ V have been highlighted on Fig. 7, and marked by a box equal to 3.1.

Compared to Fig. 6, more points are below the experimentally correct value for ITOF. This occurs at pulse lengths less than 120 s and the lower voltages (25 and

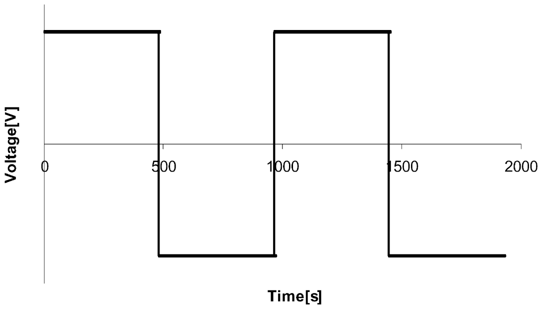


Fig. 4.

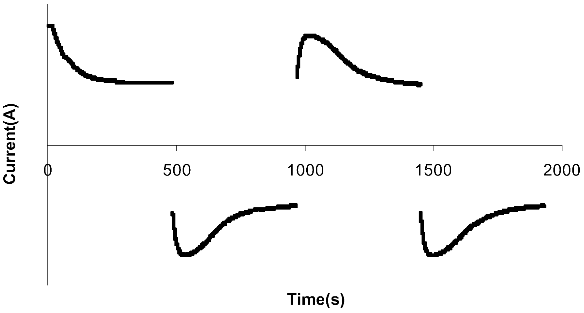


Fig. 5.

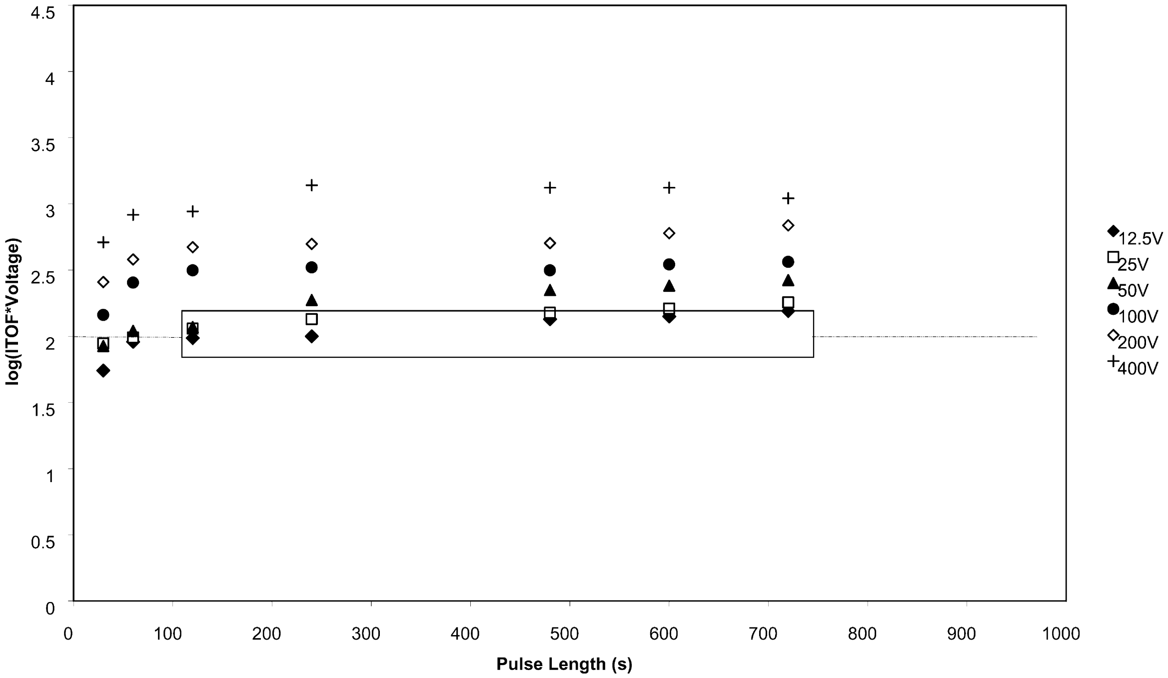


Fig. 6.

50 V). It results because this capacitor has a larger distance between the electrodes and the ions have not been pulled with a strong enough force or for a long enough time to move the required distance. Those values lying above the constant region occur at the highest voltages or longest pulse times, resulting in additional polarization and discharging effects at the electrodes.

3.2. Geometry effects

Next we examine the effect of the distance between the electrodes on selecting the proper voltage and pulse length. The capacitor has distance of 430 μm between the electrodes. This is to be compared to the smaller distance of 115 μm between the electrodes of the planar sensor.

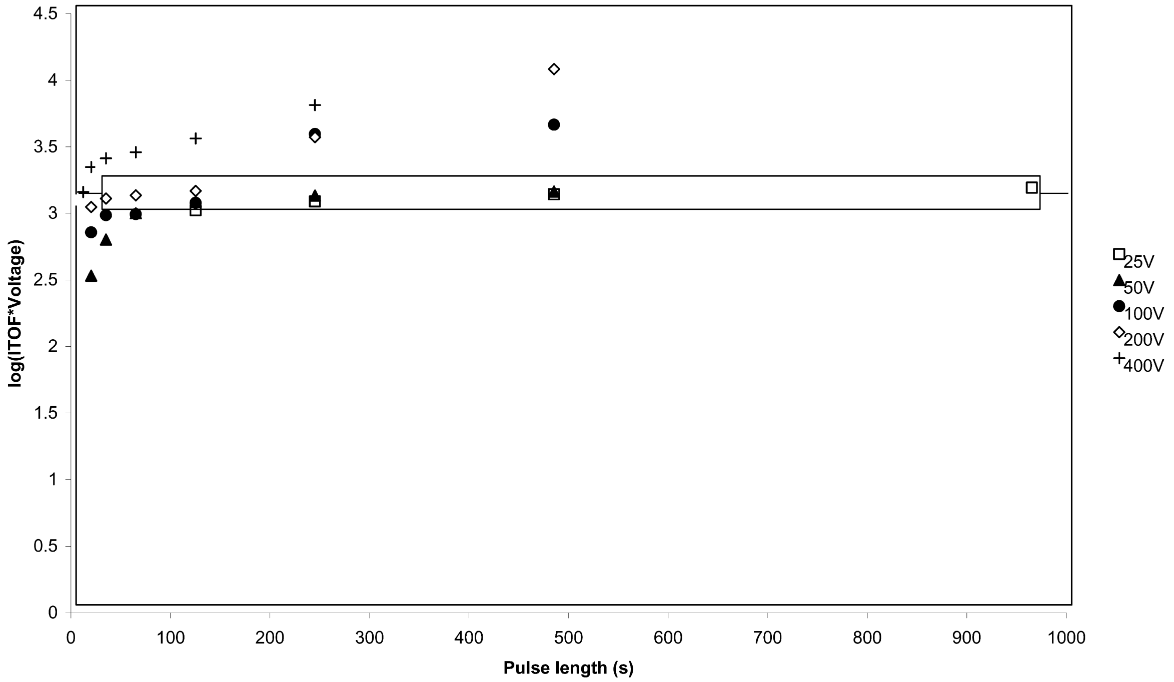


Fig. 7.

Therefore, a longer pulse length and a higher voltage is needed to pull the ions across the distance of the air capacitor's electrodes and to polarize the electrodes to an ideal level for accurate ITOF measurements. Thus, the distance between the electrodes plays an important role in selecting the correct ion mobility measurement parameters. Sensors with different distances between the two electrode plates, have thereby a different range of voltages and pulse lengths that produce good ITOF results. The ratio of the small capacitor electrode separation to the idex sensor electrode separation is 3.76, and the ratio of $d^2 = (430)^2/(115)^2$ is 13.98. Examining the plots, the constant value of log ITOF $*$ V is 3.1 at 40 °C for the capacitor. For the idex sensor the relevant value is approximately 2.0. The values of 3.1 and 2.0 are estimates obtained from the ITOF $*$ V values which show little variation with pulse length. The experimental ratio of ITOF $*$ V for the two geometries is 12.59, compared to the predicted ratio of 13.98 based on the two distances. Thus, the results show that the effects of the spacing of the electrodes of these sensor systems is as expected. Overall both the types of sensors, planar and parallel plate capacitor, provide good devices to measure the ITOF, assuming proper selection of the voltage and pulse length. Both types of capacitors follow the predicted relationship between geometry and applied field.

3.3. Evaluation of measurement precision

Since the ion concentration is constant in the dimethacrylate system, the product of ITOF, voltage, and conductivity as measured independently by an impedance analyzer should return a constant value regardless of temperature. Therefore, from Eq. (10) $t \times V \propto \mu^{-1}$.

Since $\sigma/\mu = N_i$ then

$\sigma * V * \mathrm{ITOF} = N_i$

where N_i is expected to be unchanging for D121 over the -15–100 °C temperature range and the resulting variation in viscosity. This is based on the chemical stability of this material and an absence of hydrogen bonding. When this quantity ($\sigma * V * \mathrm{ITOF}$) is plotted versus temperature, as shown in Fig. 8, there is an inherent scatter in the values in the -15–100 °C temperature range. The absence of a trend in the data indicates that the value of N_i is constant. The scatter in the results around the average value represents a measure of the range of error associated with the ITOF values. The standard deviation about the average is 9.2×10^{-9}, which is approximately a 30% uncertainty. This inherent scatter could be a limitation in the accuracy of the measurements, although a portion of this uncertainty is due to variation in environmental factors, such as the possible but certainly limited aging of the material over a long period of testing.

3.4. Viscosity and temperature dependence

Fig. 9 shows the variation of the conductivity measured by plotting the natural log of inverse dielectric measurements, the viscosity, and the value of several ITOF $*$ V measurements. All three of these quantities increase with decreasing temperature, reflecting the decrease in molecular

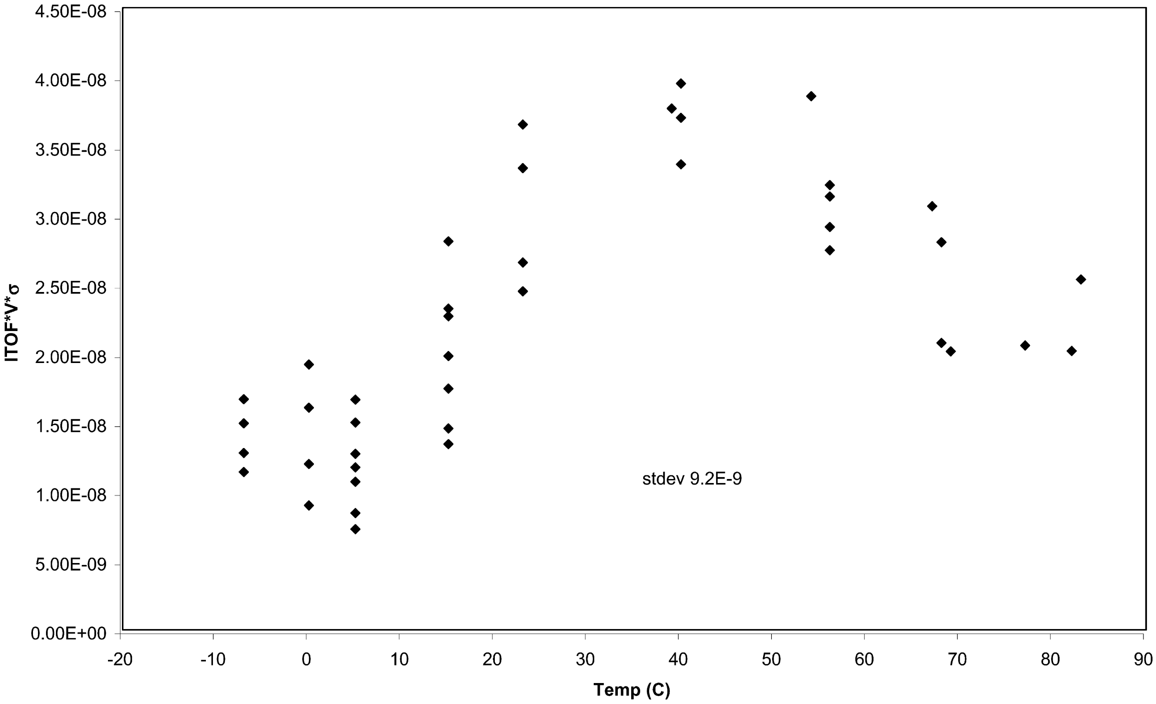


Fig. 8.

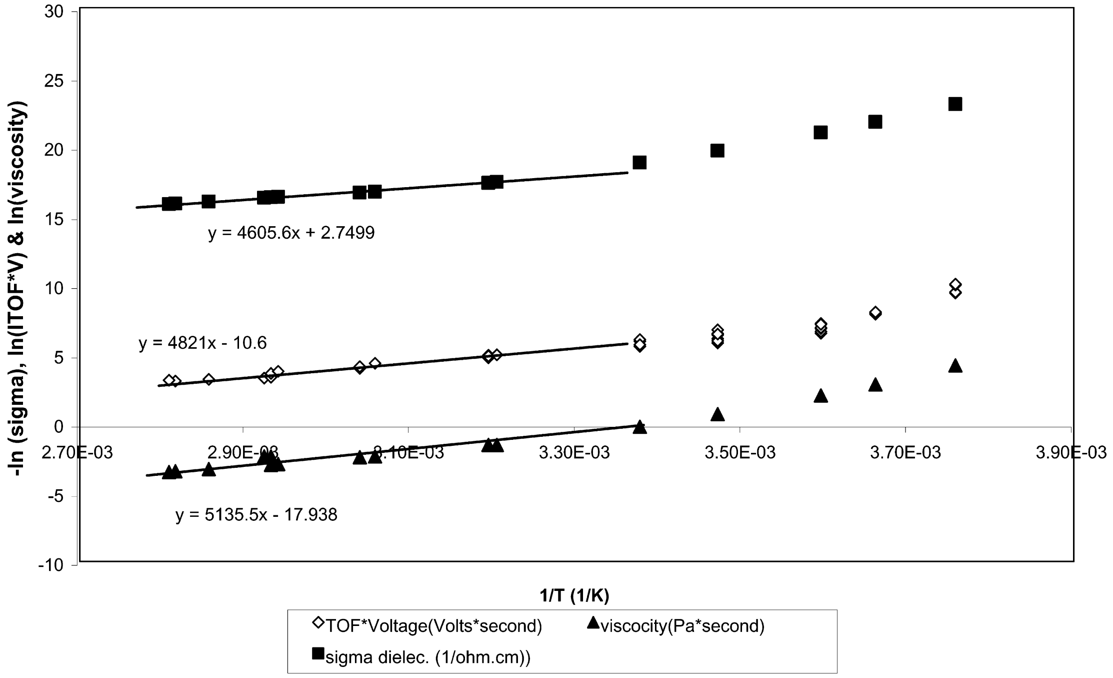


Fig. 9.

mobility with a decrease in temperature and resulting increase in viscosity. In the high temperature region, room temperature to 83 °C, a linear Arrhenius dependence for all three quantities is observed. The slopes of a linear fit to the data in this temperature region are reported in Fig. 9. As expected, when the temperature drops below room temperature, and moves into the $T_g + 50$ °C region, ($T_g \approx -48$ °C) a non-linear dependence is observed for all quantities examined.

The fact that the slopes of ITOF $* V$ (4.8) and dielectric conductivity (4.6) are close to that of viscosity (5.1) shows that the mobility of the charge carriers is almost directly inversely related to the viscosity. Comparing the slopes also confirms that experimental values for the mobility measured by the conductivity obtained using dielectrics also monitors the viscosity, as expected since the number of charge carriers in this case is constant. Comparing the ITOF $* V$ slopes with that of viscosity shows that the exponent ‘a’ in Eq. (11) is equal to 0.93.

4. Conclusions

ITOF measurements have been shown to be able to isolate and measure charge carrier mobility. But to get accurate measurements of mobility one needs to carefully select and control the field strength and pulse length. The correct pulse length and voltage need to be selected relative to the spacing of the electrodes and the viscosity of the material.

Plots of the ITOF multiplied by the applied field versus pulse length visually display the effect of not fully poling the electrodes or, alternately, creating an excessive charge polarization and discharge effect. Not allowing enough time to fully poll the electrodes results in an incorrect short value for the ITOF, while ‘over-polarizing’ the electrodes results in a longer value for the ITOF. Both of these scenarios are dependent on the variation of pulse length of applied field. Only measurements with applied fields and pulse lengths where the product is a constant provide an accurate measure of changes in mobility with changes in viscosity.

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References

[1] Kranbuehl DE. Encyclopedia of smart materials. New York: Wiley; 2002. p. 456.
[2] Kranbuehl DE. In: Runt JP, Fitzgerald JJ, editors. Dielectric spectroscopy of polymeric materials. Washington, DC: ACS; 1996. p. 303.
[3] Kranbuehl DE, Rogozinski J, Meyer A, Hoipkemeier L, Nikolic N. ACS Symp Ser 2001;141.
[4] Kranbuehl DE. Process Compos 2000;137.
[5] Kranbuehl DE, Loos A. In: Kruckenberg T, editor. Resin transfer molding for aerospace app. London: Chapman and Hall; 1998. p. 412.
[6] Lestriez B, Maazouz A, Gerard JF, Sautereau H, Boiteux G, Seytre G, Kranbuehl DE. Polymer 1998;39(26):6733.
[7] Mijovic J, Andjelic B, Fitz B, Zurawsky W, Mondragon I, Bellucci F, Nicolais L. J Polym Sci B 1996;34:379.
[8] Bellucci F, Maio V, Monetta T, Nicodemo L, Mijovic J. J Polym Sci B 1996;34:1277.

[9] Mijovic J, Andjelic S, Winnie Yee C. Macromolecules 1995;28:2797.
[10] Mijovic J, Winnie Yee C. Macromolecules 1994;27:7287.
[11] Bellucci F, Maio V, Monetta T, Nicodemo L, Kenny J, Nicolas L, Mijovic J. J Polym Sci B 1994;32:2519.
[12] Mijovic J, Kenny J, Nicolais L. Polymer 1993;34:207.
[13] Zukas WX, Wentworth SE. Polym Compos 1987;8:232.
[14] Mijovic J, Fitz BD. Novocontrol: application note dielectrics 2; 1999.
[15] Day DR. Polym Engng Sci 1989;29:334.
[16] Day DR, Shepard DD. Polym Compos 1991;12:87.
[17] Ciriscioli PR, Springer GS. SAMPE J 1989;25:35.
[18] Day DR, Lewis T, Lee HL, Senturia SD. J Adhes 1985;18:73.
[19] Sanjan ZN. Polym Engng Sci 1986;26:373.
[20] Companik JE, Bidstrup SA. Polymer 1994;35(22):4834.
[21] Bidstrup SA, Simpson JO. J Polym Sci B 1995;33:43.
[22] Simpson JO, Bidstrup SA. J Polym Sci B 1995;33:55.
[23] Gallone G, Capaccioli S, Levita G, Rolla PA, Corezzi S. Polym Int 2001;50(5):545.
[24] Cortaberria G, Arruti P, Mondragon I. Polym Int 2001;50(9):957.
[25] Tombari E, Ferrari C, Salvetti G, Johari GP. J Phys: Condens Matter 1997;9(33):7017.
[26] Eloundou JP, Ayina O, Nga NH, Gerard JF, Pascault JP, Boiteux G, Seytre G. J Polym Sci B 1998;36:2911.
[27] Eloundou JP. Eur Polym J 1999;35:1473.
[28] Eloundou JP, Ayina O, Gerard JF, Pascault JP. Polym Prepr ACS Div Polym Chem 2000;41(1):752.
[29] Maistros G, Block H, Bucknall C, Partridge I. Polymer 1992;33:4470.
[30] Friedrich K, Ulanski J, Boiteux G, Seytre G. IEEE Trans Dielec Elec Insul 2001;8(3):572.
[31] Friedrich K, Vinh-Tung C, Boiteux G, Seytre G, Ulanski J. J Appl Polym Sci 1997;65:2529.
[32] Ulanski J, Friedrich K, Boiteux G, Seytre G. J Appl Polym Sci 1997; 65:1143.
[33] Tournilhac F, Bassoul P, Barnik MI, Blinov LM. Mol Mater 1998;9: 271.
[34] Seanor DA, editor. Electrical properties of polymers. New York: Academic Press; 1982.
[35] Winokur PS, Roush M, Silverman S. J Chem Phys 1975;63(8):3478.
[36] Vojnovic B, Visscher KJ. Radiat Phys Chem 1991;38(3):349.