Electrical conduction in polyetherimide

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Electrical conduction characteristics in polyetherimide (PEI) have been investigated at electric fields of 0.9–27 MV/m over temperatures of 50–100 °C. It is found that the current density of PEI increases with the increase of electric field and temperature and that its conduction is governed by the thermally activated ion hopping process. The hopping distance of ions in the PEI decreases from 5.69 nm at 50 °C to 3.34 nm at 100 °C due to the increase of chain motion with the increase of temperature. The activation energy for the electrical conduction is 0.74 eV. © *1996 American Institute of Physics.* [S0021-8979(96)02323-7]

I. INTRODUCTION

Recently great attention has been paid to a search for insulating materials which can be used at high temperatures and/or under gas environment. However, most research was centered at the polymers such as polyethylene and polypropylene which cannot be used at high temperatures. Some reports can be found in the literature on the electrical properties of high-temperature plastics such as polyimide (PI), polyethersulfone (PES), polyetheretherketone (PEEK), and aromatic liquid crystals.[1–7]

Polyetherimide (PEI) is one of the high-temperature plastics which has a high glass transition temperature (about 220 °C) and good mechanical properties.[8] Since it can be processed relatively easily, it is one of the engineering plastics which can be used as an insulating material for high-temperature purposes under gas environment.

In this work, the electrical conduction characteristics of PEI were studied at electric fields of 0.9–27 MV/m over the temperatures of 50–100 °C.

II. EXPERIMENTAL PROCEDURES

Ultem 1000 of GE Plastic Co. was used as a PEI sample and its chemical formula is shown in Fig. 1. This PEI has a bisphenol-A linked with aromatic imide groups.

The PEI films of 100 μm thickness were prepared by solvent casting using CH_2Cl. The solvent casted films were treated in a vacuum oven to remove residual CH_2Cl and then compression molded using a hot press at 250 °C to prepare 50 μm thick films. These films were cleaned with a fresh ethanol several times and then silver was vacuum evaporated on its surfaces. The thickness of silver electrodes was about 0.3 μm.

The apparatus used to measure the conduction currents is composed of a power supply ($\pm$3 kV dc, Keithley 247), electrometer (Keithley 617), and test cell. The test cell contains a measuring electrode, the counter electrode, and a guard ring. The diameter of measuring electrode was 28 mm. The current as a function of time was transferred to the personal computer via a general purpose interface board (GPIB) and stored in a diskette. The temperature of 50–100 °C was controlled in an air convection oven. The sample was thermally equilibrated for about 12 h at the test temperatures before tests and one sample was used for all tests.

III. RESULTS AND DISCUSSION

Figure 2 shows the currents at 100 °C as a function of time at various electric fields and Fig. 3 shows the currents at 25 MV/m as a function of time at 50, 85, and 100 °C. From these two figures, it can be observed that the currents decrease as a function of time. The currents of PEI is in the range of 10^{-11} A at 100 °C over the electric fields of 7–27 MV/m and increase with the increase of temperature. Since the change of currents as a function of time appeared more or less stabilized after about 1000 s after the voltage application, the currents after 1800 s were taken as isochronal currents.[9] From a separate test on the frequency dependence of the capacitance and dissipation factor, a dielectric relaxation frequency was found to be 0.9 MHz which corresponds to about 1 μs in a time scale. This means that the polarization of dipoles or ions is completed in this time scale and that the current change with time shown in Figs. 2 and 3 are the leakage currents.

Figure 4 shows the isochronal current density (J) increases with the increase of electric fields (E) at all temperatures. The suppression of the rate of change of current density at certain electric fields found frequently in polyethylene and polypropylene was not found in this sample.[9,10]

Measurements of complex impedance is one of the ways to determine whether the conduction mechanism is electronic or not. The measurement of complex impedance for the frequency range of 1 kHz–5 MHz showed a semicircle, which indicates that this sample does not obey the electronic process. This fact suggests that the conduction in the PEI is governed by an ionic conduction mechanism, as observed in many engineering plastics such as PEEK and PES.[2–4] It is a conduction mechanism where the ions existing in the polymers are thermally activated and participate in the conduction process.

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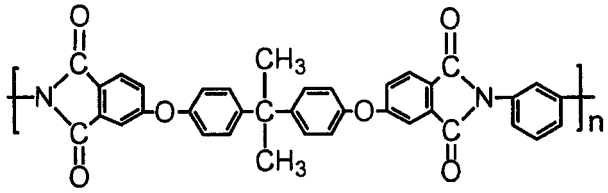

FIG. 1. Chemical structure of PEI.

When ions are hopping by a thermally activated process, current density J is expressed as Eq. (1):

$$J=2n\alpha\nu\ \exp(-U/kT)\sinh(eE\alpha/2kT), \tag{1}$$

where e, n, α, ν, U, k, and T are the charge of electron, carrier density, hopping distance, attempt to escape frequency, activation energy, Boltzmann constant, and absolute temperature. This expression proposed first by Mott and Gurney[11] can be modified as Eq. (2) at high electric fields:[12]

$$J=n\alpha\nu\ \exp(-U/kT)\exp(eE\alpha/2kT). \tag{2}$$

In Eq. (2), $\exp(-U/kT)$ is independent of the electric field and can be treated as a constant with respect to electric field. It is also an intercept in a log J vs E plot.

Using Eq. (1), the hopping distance can be estimated from a curve fitting between the current density and sinh term. The hopping distances estimated by this method are 5.69 nm for 50 °C, 4.01 nm for 85 °C, and 3.34 nm for 100 °C. These values show that the hopping distance decreases with the increase of temperature, which can be attributed to the increase of chain motion with the increase of temperature. The current density as a function of the electric field can be calculated by Eq. (2) using these hopping distances. Figure 5 shows the measured data and the theoretical curves estimated by particular hopping distances.

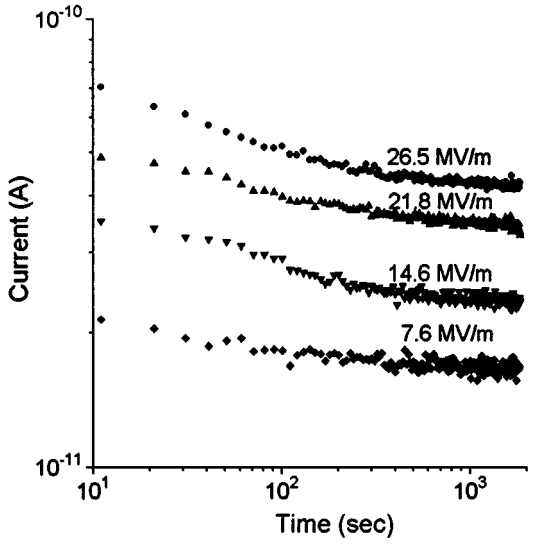

FIG. 2. Conduction currents at 100 °C as a function of time at various electric fields.

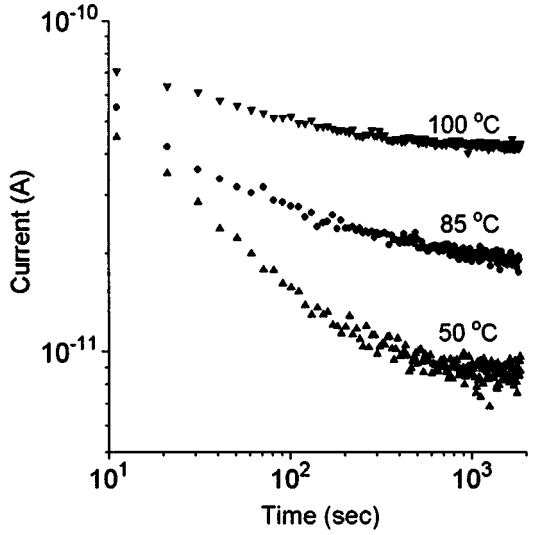

FIG. 3. Conduction currents at 25 MV/m as a function of time at various temperatures.

Both Schottky and Poole–Frenkel mechanisms were also examined as follows. The Schottky mechanism is an electrode-limited conduction process and can be expressed by the following equations:[13]

$$J=AT^2\ \exp(-\varphi/kT)\exp(\beta_S E^{1/2}/kT), \tag{3}$$

$$\beta_S=(e^3/4\pi\epsilon\epsilon_0)^{1/2}, \tag{4}$$

where J, φ, β_S, ϵ, and ϵ_0 are the current density, barrier height between the electrode and sample, Schottky coefficient, relative permittivity, and permittivity in vacuum. The Poole-Frenkel mechanism can be expressed by the following equations:[13]

$$\sigma=\sigma_0\exp(\beta_{\mathrm{PF}}E^{1/2}/kT), \tag{5}$$

$$\beta_{\mathrm{PF}}=(e^3/\pi\epsilon\epsilon_0)^{1/2}, \tag{6}$$

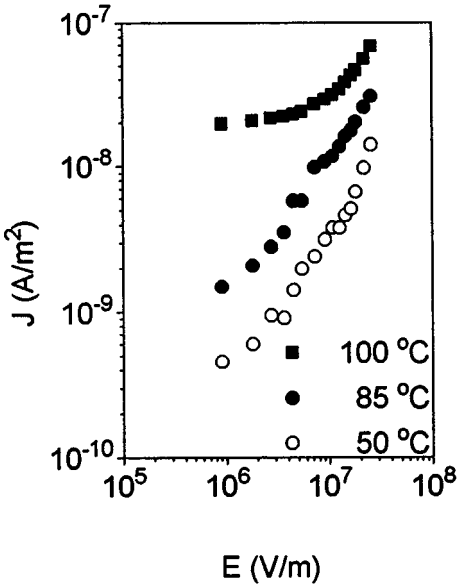

FIG. 4. $J-E$ curves of PEI after 1800 s.

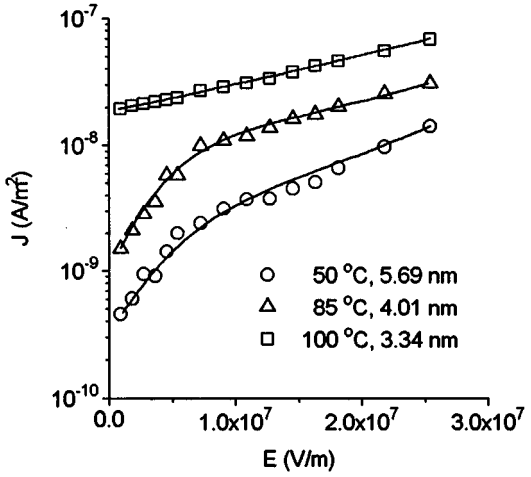

FIG. 5. Comparison of measured and calculated current densities as a function of electric fields: Measured data (symbols), calculated data (solid line).

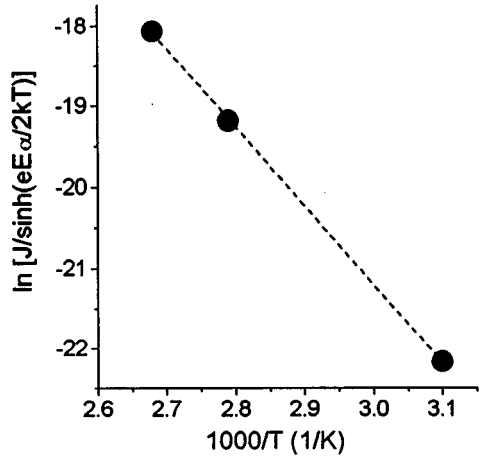

FIG. 6. Temperature dependence of current densities in PEI.

where σ and β_{PF} are the conductivity and Poole-Frenkel coefficient. The method to use these equations for the examination of conduction mechanisms is as follows: First, one obtains the coefficients from the slope of log J vs $E^{1/2}$ plots in the case of Schottky mechanism and log σ vs $E^{1/2}$ in the case of Poole-Frenkel mechanism. Then, the dielectric constants of the sample are estimated from these coefficients. If these relative permittivities agree with the literature values, it can be said that the sample follows the corresponding conduction mechanisms.

The dielectric constants calculated from a Schottky plot were 3.5 at 50 °C, 5.59 at 85 °C, and 8.60 at 100 °C, which are high compared to those of literature value of dielectric constant, 3.1 for PEI.[8] Since the dielectric constants by a Poole-Frenkel mechanism is twice of those by a Schottky mechanism [Eqs. (4) and (6)], the Poole-Frenkel mechanism can be automatically excluded.

To examine whether or not the conduction process changes, $\ln[J/\sinh(eE\alpha/2kT)]$ was plotted as a function of $1/T$ in Fig. 6. A linearity is observed in this figure, which implies that the conduction mechanisms did not change at this temperature range, which is quite reasonable since the range of test temperature is below the T_g of PEI. The activation energy was calculated from the slope in Fig. 6 to be 0.74 eV.

Ionic hopping conduction in engineering plastics such as PEEK and PES is known to originate from the ionic impurities such as the reaction residuals and the moisture also contributes to the ionic conduction.[3,4] However, the sources of ionic conduction in the PEI used in this study are not known at this moment. More work is needed to get information on this.

IV. CONCLUSIONS

Electrical conduction in PEI was governed by the thermally activated ionic hopping process at the temperature up to 100 °C over the electric fields of up to 27 MV/m. The hopping distances decreased from 5.69 nm at 50 °C to 3.34 nm at 100 °C, which was attributed to the increase of chain motion with the increase of temperature. The conduction process did not change at this temperature range and the activation energy for the electrical conduction was calculated to be 0.74 eV.

ACKNOWLEDGMENT

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