The Conduction Characteristics in Oriented Polypropylene Films

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The conduction characteristics in Oriented Polypropylene (OPP) film were studied over electric field intensities between 10 MV/m and 300 MV/m. The range of the conduction characteristics was divided into five regions with increasing field intensity. Particularly, in the region from 70 MV/m to 82 MV/m voltage-controlled negative resistance was displayed. In the negative resistance region, current oscillations were also observed. The negative resistance characteristics could be explained by Gibbons' theory.

Keywords : polypropylene, negative resistance, current oscillation, poole-frenkel, schottky

1. INTRODUCTION

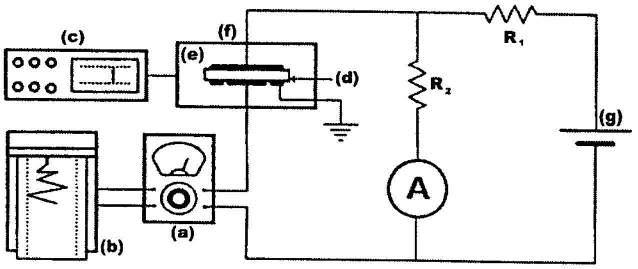
Non-polar polymers such as polypropylene(PP) have been widely used as insulating materials for power capacitors because of their low dielectric losses and superior breakdown strength.[1] Many studies on electrical conduction characteristics of PP films, including the relationship between their morphology and chemical structure, have been made, K. Sakaoku [2] has observed electron microscopy of drawn PP, K. Ikezake, et al. [3] has studied the effect of crystallinity on electrical conduction in PP, P. J. Phillips [4] has investigated some morphology-electrical property relationships between polymers, and T. Umemura [5] and K. Abe, et al. [6] have studied the influence of thermal-aging on morphology and electrical properties of biaxially-oriented PP(OPP) films. It is known that the morphology of polymers has significant effects on their conduction process and, among others the mechanical drawing of PP film improves its crystallinity and electric strength.

Some investigators have observed negative resistance and current oscillations in the electrical conduction of polymer materials such as polystyrene, [7] polyethylene [8] and polymethyl-methacrylate (PMMA). [9],[10] In spite of all these studies, the electric behavior and the electrical conduction of polymer materials are still not sufficiently understood. [1],[3],[5] Generally, it is more difficult to interpret conduction mechanisms occurring in OPP films due to their high volume resistance and very low carrier density. Only a few papers [11],[12] have dealt with the electrical conduction in OPP films, and little discussion on negative resistance and current oscillation phenomena has been carried out. In this paper, we investigate the influence of electric strength and temperature on electrical conduction in oriented polypropylene; special attention has been paid to the existence of negative resistance and current oscillations. The characteristics of negative resistance are also discussed on the basis of theory. [13]

2. EXPERIMENTAL

Commercially available oriented polypropylene (OPP, 15 μm in thickness) films were used in this work. The oriented polypropylene was made by the 'Tenter' type orientation, in which the machine direction (MD, 450%) and the transverse direction (TD, 800%) orientations are obtained at temperatures between 150°C and 160°C. Before the electrical measurements were made, the X-ray diffraction patterns of the samples by using Rigaku (Model D/Max-III A) showd to be about 80% crystallized. The OPP samples were cut into 100 mm diameter circles and were cleaned in benzene. The samples were later covered with aluminum plates and inserted into the electrodes which was located in pure paraffin oil. The DSC fusion curves of OPP film were measured using a Perkin Elmer International Company instrument (Model 3600). The melting points were found to be around 168°C for OPP films.

A schematic diagram of the experimental apparatus is shown in Fig. 1. DC voltage was supplied from a DC HV generator. The conduction current flowing through the samples was measured by an electrometer (Keithley Instrument 602, USA) and recorded by a chart recorder (J.J.CR 503, UK). The brass disk electrodes were 50 mm diameter. The guard-ring had 70 mm inner diameter and 90 mm external diameter. Two very high resistances (R_1=2,970 MΩ, R_2=4,500 MΩ) were used in order to control the current following through the tested samples and to regulate the voltage across the samples. The experimental cells were enclosed by a grounded copper screen box and located in an oven. The temperature in the oven was regulated by a temperature controller, and the sample temperature was measured with a thermocouple attached to the sample. The test sample was located in a glass container filled with paraffin oil to eliminate partial discharge.



(a) electrometer (b) recorder (c) temperature controller
(d) specimen (e) oil (f) cell
(g) DC power supply (0~50 kV)

Fig. 1. Block diagram of experimental apparatus

3. Results and Discussion

3.1. Conduction Current in OPP Film

The conduction current depends on the temperature and electric stress. Results of measurements are given in Fig. 2, which shows the conduction current of the OPP film at constant temperature (15°C and 25°C) as a function of electric field stress. The relationship between conduction current and electric field is not linear, i.e., non-ohmic. Five different regions, region I, II, III, IV, and V, may be distinguished in the diagram. Region I is below 40 MV/m, region II is between 40 MV/m and 70 MV/m, region III is from 70 MV/m to 82 MV/m, region IV is between 82 MV/m and 240 MV/m and region V is above 240 MV/m.

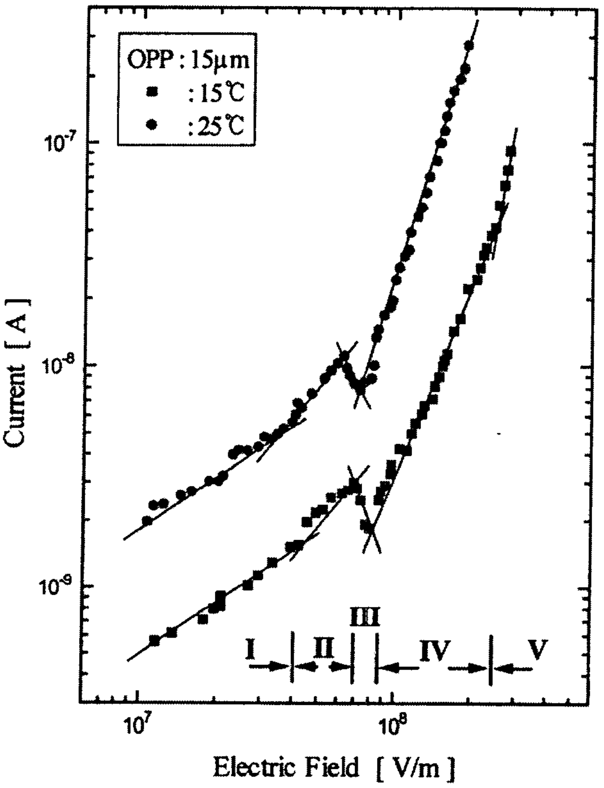


Fig. 2. Conduction current as a function of electric field at temperatures of 15°C and 25°C in OPP film, thickness 15μm and diameter 50nm.

3.2. Conduction Mechanism in Region I, E < 40 MV/m

The ohmic conduction mechanism in polymers has been studied by many researchers. Lamb, et al. [11] and Lamper [12] found that in the ohmic region of conduction in polymer materials, the diffusion current generally may be disregarded because it is such a small value. Our measurements in region I, field stress below 40 MV/m

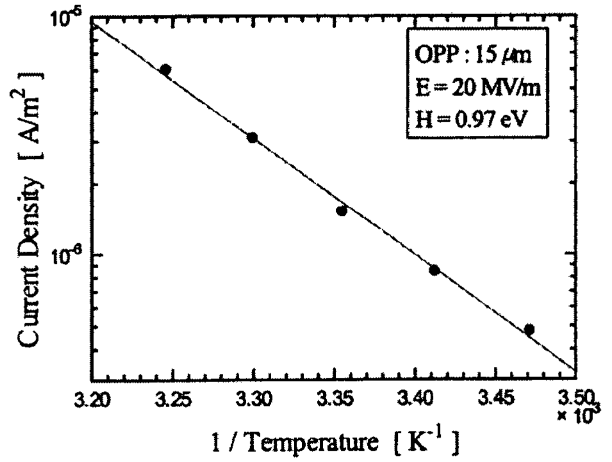


Fig. 3. Plot of the conduction current versus inverse temperature in the ohmic region

and 15°C, support the ohmic conduction mechanism theory. Fig. 3 is the Arrhenius plots of log I at steady state versus 1/T for region I of Fig. 2. The activation energy obtained from the diagram is around 0.97 eV. Similar values have been obtained by other workers. [10],[14] The carriers attributed to the conduction current may be due to ionic impurities. Carriers such as free radicals may be formed in the material during the processing of the polymer.

3.3. Conduction Mechanism in Region II, 40 MV/m < E < 70 MV/m.

Fig. 4 was obtained from Fig. 2 and shows the relationship between the conductivity and electric field as a function of $\log\sigma$ versus $E^{1/2}$. Thus Poole-Frenkel or Schottky conduction mechanisms might be operative in this region.

Charge injected from a metal to an insulator at medium fields may take place by field-assisted thermioinic emission, a process known as Schottky emission. The force exerted on a particle at a distance x from the interface is given b

$$F = eE - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r(2x)^2} \tag{1}$$

The work done on the particle is

$$W = -\int f dx = -eEx - \frac{e^2}{16\pi\varepsilon_0\varepsilon_r x} + \phi \tag{2}$$

The constant of integration has been chosen so that $W \equiv \phi$ at a large distance from the electrode under zero applied field. For nonzero field, W has a maximum value ϕ_{app} at the point where $F = 0$. This gives the result

$$\phi_{\text{app}} = \phi - \beta_S E^{1/2} \tag{3}$$

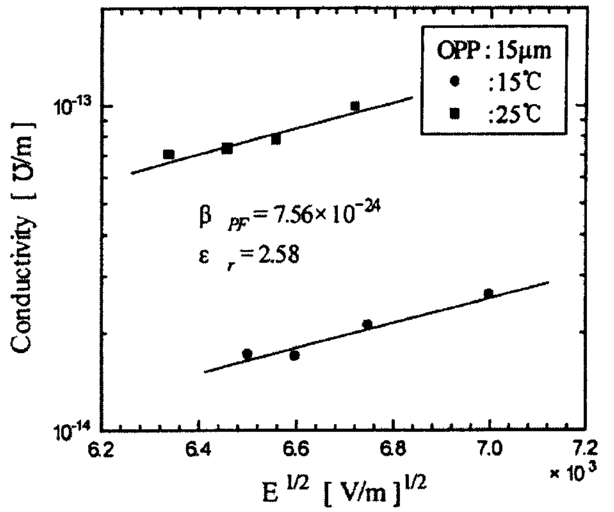


Fig. 4. Plot of $\log\sigma$ versus E$^{1/2}$ in the Poole-Frenkel region

where,

$$\beta_S = \left(\frac{e^3}{4\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \tag{4}$$

Consequently, the current density drawn over this barrier is

$$J_S = AT^2 \exp\left(-\frac{\phi}{kT}\right)\exp\left(\frac{\beta_S E^{1/2}}{kT}\right) \tag{5}$$

where $A = 12\times10^5 in[A/m^2k^2]$, ϕ is the potential barrier, ε_r is the dielectric constant at high frequency, and T is the absolute temperature. When an electric field interacts with the coulombic potential barrier of trap the height of the barrier is lowered. This process known as Pool-Frenkel effect is the bulk analogue of the Schottky effect at an interfacial barrier. Since the potential energy of an electron in a Coulombic field, $-e^2/4\pi\varepsilon_0\varepsilon_r$, is four times that due to image force effects, the Pool-Frenkel attenuation of a Coulombic barrier, ϕ_{PF}, in a uniform electric field is twice that due to the Schottky effect at a neutral barrier.

$$\Delta\phi_{PF} = \left(\frac{e^3}{\pi\varepsilon_0\varepsilon_r}\right)^{1/2} E^{1/2} \equiv \beta_{PF}E^{1/2},$$

$$\beta_{PF} = \left(\frac{e^3}{\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \tag{6}$$

Thus, the conductivity is field-dependent and the current density drawn over this barrier is

$$J_{PF} = J_0 \exp\left(-\frac{\phi}{2kT}\right)\exp\left(\frac{\beta_{PF}E^{1/2}}{2kT}\right) \tag{7}$$

For deciding whether it is Poole-Frenkel or Schottky process, [15],[16] the slope of the straight lines of the plots(Fig. 4) are compared with the theoretically calculated slopes (β_{th}) using the Schottky relationship; $\beta_s = \left(e^3/4\pi\varepsilon_0\varepsilon_r\right)^{1/2}$. In the case of our sample, the theoretical value (β_{th}) of β_s is 3.95×10^{-24} (using $e = 1.6 \times 10^{-19}$ coul, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, and $\varepsilon_r = 2.36$ obtained from the dielectric measurement). If the value of β obtained from the slope is close to it of β_{th} obtained theoretically, the process is that of Schottky emission. On the other hand, if the value of β obtained from the slope is double that of β_{th}, the process is that of Poole-Frenkel emission. [15],[17]

From the slope of the straight line in Fig. 4, we found that β_{PF} was 7.56×10^{-24} and ε_r was 2.58, respectively. These results are similar to the values presented by Brandrup. [18] The Arrhenius plot for a field of 44 MV/m is shown in Fig. 5. The barrier height value was found to be $\phi = 3.03$ eV. Toureille [10] proposed that region II in polyethylene might be controlled by the Schottky effect. In our study, the value of β_{PF} is double that of the theoretically calculated $\beta_{th}(= 3.95 \times 10^{-24})$ and $\beta_S(= 3.76 \times 10^{-24})$ which was obtained in region IV; $\beta_{PF} = 7.56 \times 10^{-24} \fallingdotseq 2 \times 3.95 \times 10^{-24}(2\beta_{th}) \fallingdotseq 2 \times 3.76 \times 10^{-24}(2\beta_S)$. Therefore, the conduction mechanism in region II is likely to be dominated by the Poole-Frenkel effect.

3.4. Conduction Mechanism in Region III, 70 MV/m < E < 82 MV/m

Region III of Fig. 2 shows a voltage-controlled negative resistance. This negative conduction phenomena for OPP film was observed between an electric field stress of 70 and 82 MV/m at 15°C. In the negative resistance region III, a current oscillation phenomena was also observed. This oscillation phenomena was found by Weinreb, et al. [7] in polystyrene, by Swan [8] in polyethylene and by Toureille [10] in polymethylmethacrylate, polyethylene and polystyrene. Fig. 6 shows the negative resistance data obtained as a function of temperature in range from 15°C to 55°C, and electric field stress between 10 and 300 MV/m in OPP film. It may be observed that as the temperature is increased above 25°C, the entire current versus electric field stress plot is shifted gradually towards low field intensity and the magnitude of the current increases.

The appearance of the negative resistance means a decrease in one of the parameters controlling conductivity ($\sigma = ne\mu$, where n is carrier number density, e is the charge of electron and μ is the mobility) with increasing electric field strength. According to some workers, [5],[6],[10] the charge density remains constant (n is still limited due to the barrier effect); therefore, the negative resistance must be due to a decrease in the mobility of the carriers.

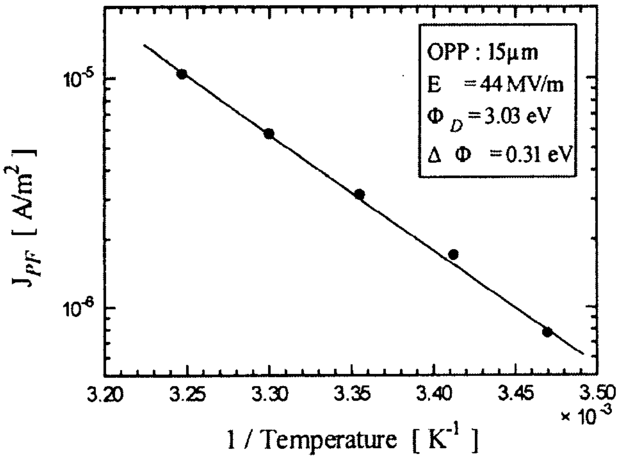


Fig. 5. Plot of J_{PF} versus 1/T in the Poole-Frenkel region

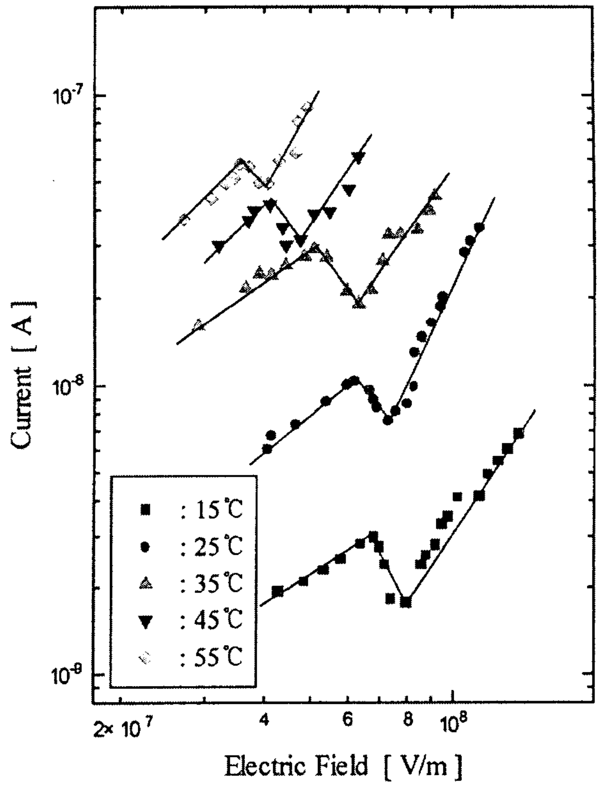


Fig. 6. Characteristics of negative resistance observed at various temperatures in OPP film with 15μm thick

According to Gibbons' theory, [13] the temperature of electrons is higher than that of the lattice with increasing electric field. This is because the electric field accelerates the electrons and increases their kinetic energy beyond what they would have if they were in thermal equilibrium with the lattice. In this case, these energetic and hot electrons will relax back and lose their excess energy by colliding with the lattice. Therefore, the maximum value of drift velocity (V_d) would be subject to the restriction due to thermo-kinetic velocity (V_{th}) by the following equation:

$$V_d = V_{th}\{1-\exp(-E/E_c)\} \qquad (8)$$

where E is the applied field and E_c is the critical field. The assumption is made that the drift velocity has a constant value during negative resistance. If the critical field is constant, the thermo-kinetic velocity is $(3kT/m)^{1/2}$, where m is the mass of the electron, k is Boltzman's constant and T is the absolute temperature. Therefore, equation (8) gives

$$V_d = C/T^{1/2} = \{1-\exp(-E_n/E_c)\} \qquad (9)$$

where C is a constant, and E_n is the applied electric field in the negative resistance region. We expect from equation (9) that increasing the temperature causes a decrease in the field strength where negative resistance occurs, E_n. To consider the change of the negative resistance with temperature, one may write equation (9) in the form below ;

Squaring both sides of equation (9) yields;

$$\frac{const}{T} = \{1-\exp(-E_n/E_c)\}^2 \text{ and}$$

$$T = const(\exp E_n/E_c - 1)^{-2} \text{ or}$$

$$\ln T = -2\ln(\exp E_n/E_c - 1) \qquad (10)$$

$$\frac{\Delta T}{T} = \frac{-2\frac{\Delta E_n}{E_c}}{(\exp E_n/E_c - 1)} \qquad (11)$$

Therefore, we find:

$$\Delta E_n = \frac{\Delta T E_c(\exp E_n/E_c - 1)}{-2T}$$

$$= -\frac{\Delta T E_c(\exp E_n/E_c - 1)}{2T} \qquad (12)$$

If exp $E_n/E_c \gg 1$, the above equation is:

$$\Delta E_n = -\frac{\Delta T E_c \exp E_n/E_c}{2T} = \frac{\Delta T E_c \exp(-E_n/E_c)}{2T}$$

$$= \frac{\Delta T E_c}{2T\exp E_n/E_c} \qquad (13)$$

For example from Fig. 6, the experimental error of V_d/V_{th} is estimated to be 4%:

Table 1. Electrical field at which negative resistance appears in OPP film

field / T [°C]	Electric field [MV/m]	
	Experimental	Theoretical
15	70	-
25	61	60.89
35	52	53.20
45	44	45.66
55	38	38.03

$$\exp(E_n/E_c) = 0.04, \text{ and } \frac{E_n}{E_c} = \ln 0.04 \qquad (14)$$

$$\text{so } E_c = \frac{E_n}{3.22} \qquad (15)$$

$$\therefore \exp(-E_n/E_c) = \exp\left(\frac{E_n}{E_c}\right)^{-1} = (0.04)^{-1} \qquad (16)$$

For 15°C, 70 MV/m (Reference): From Equation (13)

$$\Delta E_n = \frac{\left(-\frac{70\times10^6}{3.22}\right)\times(25C-15C)\times(0.04)^{-1}}{2\times(273+25)}$$

$$= -9.11\times10^6 = -9.11 \text{ MV/m} \qquad (17)$$

For 25°C, 60.89 MV/m: E = (70 - 9.11) ×10^6 = 60.89×10^6 = 60.89 MV/m

$$\Delta E_n = \frac{\left(-\frac{61\times10^6}{3.22}\right)\times(35C-25C)\times(0.04)^{-1}}{2\times(273+35)}$$

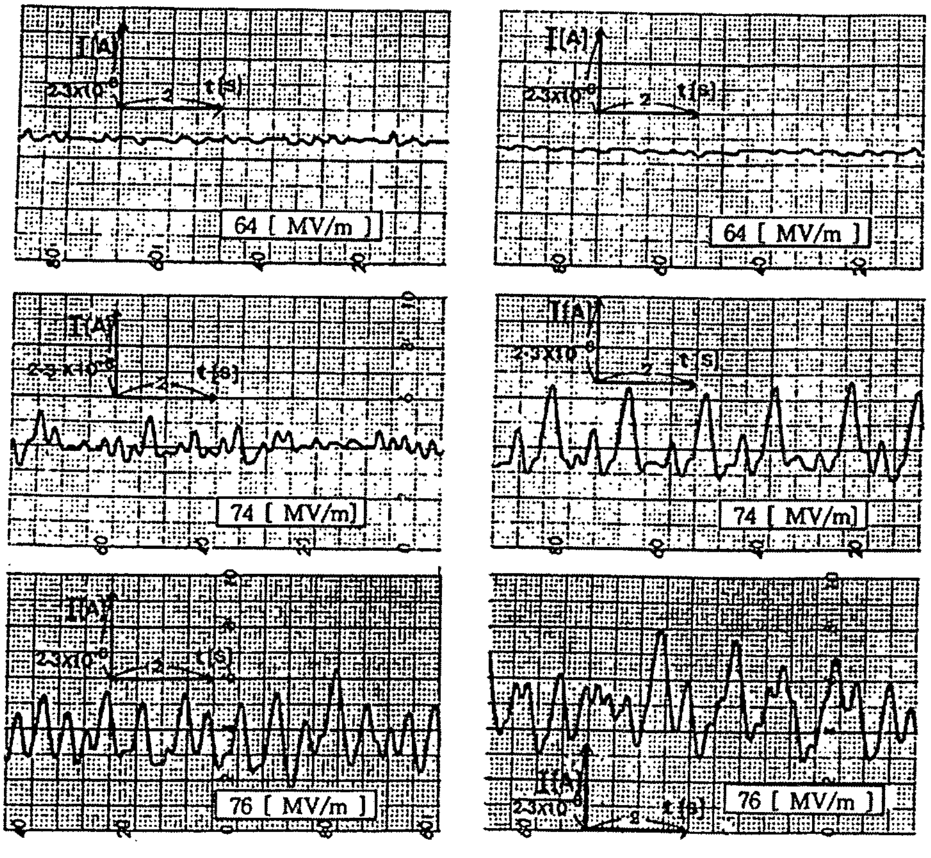
$$= -7.69\times10^6 = -7.69 \text{ MV/m.} \qquad (18)$$

The field value of the negative resistance region was obtained experimentally and compared with the calculated value from equation (13), and Table 1 shows that excellent agreement was found between the experimental and theoretical values.

The electric field (E_n) at which negative resistance occurs, becomes gradually lower with increasing temperature above 15°C. This may be explained from equation (9). If the critical field is constant, an increase of the temperature decreases E_n.

3.5. Oscillation of Conduction Current in OPP Film

The characteristics of the current oscillation depend strongly on the applied electric field, temperature, and crystallinity of the material. Fig. 7 shows the current oscillation in OPP films at electric stresses between 64 ~



(a) 15°C (b) 25°C

Fig. 7. Current oscillation observed at electric stress between 64~76 MV/m in OPP film with 15μm thick

76 MV/m and at temperatures between 15°C and 25°C as a function of time for OPP films. The current oscillation appeared in region III, where negative resistance exists. Especially, the oscillations may be clearly observed at the beginning and end points of region III (Fig. 2). At the beginning point of region III, the emission of contact becomes stranger than the flow of carriers in the bulk of the sample and a certain number of extra carriers is injected into the material. These charges flow very slowly because a large number of traps in the sample are going to cause the fall of the field at the injection electrode to below its initial value.

As a result, the injection is blocked and a pack of injected charges travels through the sample without a dispersion. When this accumulation domain is collected by the other electrode, the field returns to its initial value at the contact, the latter being able to inject a fresh charges. This phenomena reveals itself in the appearance of regular peaks during the recording of current along with time.

Fig. 7 (a) shows the current oscillation in OPP versus the electric field at 64 MV/m, 74 MV/m, 76 MV/m and at a temperature of 15°C. The current oscillation observed at an electric field 64 MV/m occurs just before the negative resistance appears. Fig. 7 (b) shows the current oscillation in OPP versus the electric field at 64 MV/m, 74 MV/m, 76 MV/m and at a temperature 25°C in OPP film. The magnitude of current oscillation gradually increases with increasing electric field strength and temperature. The current oscillation has a repetition rate of 0.67 Hz at an electric field of 74 MV/m and at a temperature of 25°C in Fig. 7 (b). However, the period of current oscillations decreased as the applied voltage stress increased.

In our results, at temperatures of 25°C, 35°C and 45°C and different field stress, the current oscillations were very similar to the results presented by Toureille. [10] From Fig. 7, at field stress of 74 MV/m and a temperature of 25°C, we caculated the mobility of carriers to be 1.44×10^{-13} $m^2/V\cdot s$ in OPP. This value agrees with given 1×10^{-13} $m^2/V\cdot s$ by Toureille [10] and 4×10^{-13} $m^2/V\cdot s$ by Bremmer and Pinnow in polyethylene film. [19]

3.6. Conduction Mechanism in Region IV, 82 MV/m < E < 190 MV/m

The conduction mechanism in oriented polypropylene was also studied in a high electric field. The conduction current obtained at temperatures from 5°C to 25°C are presented in Fig. 8. In this region, Poole-Frenkel or

Schottky conduction mechanisms might be operative as in region II.

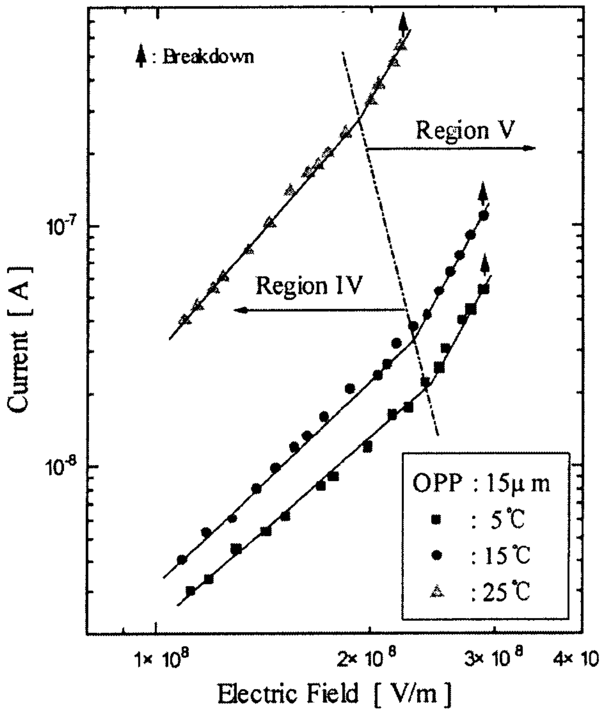


Fig. 8. Conduction current at high field over 100MV/m

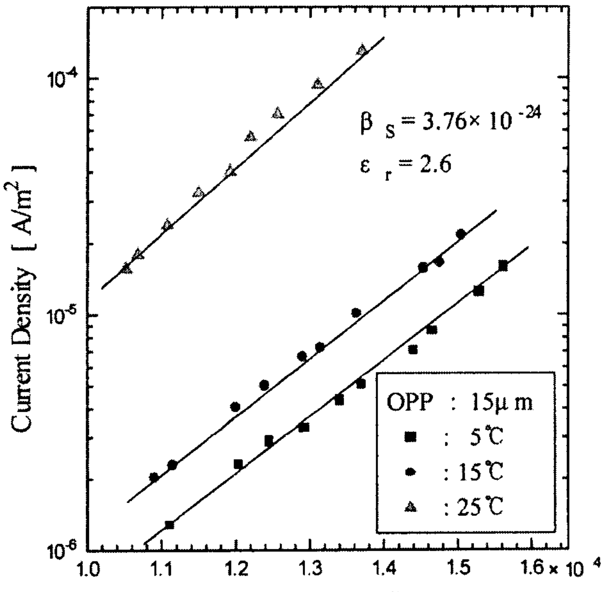


Fig. 9. Plot of J_S versus $E^{1/2}$ in the Schottky region

Fig. 9 presents log J_s versus the square root of applied field. From the slope of Fig. 9, $\beta_s = 3.76\times10^{-24}$ and $\varepsilon_r =$ 2.6 were calculated. The slope β_s obtained in this region is close to β_{th} $(=3.95\times10^{-24})$ caculated theoretically, and equal to half of the slope β_{PF} (= 7.56×10^{-24}) for the Poole-Frenkel effect. From the results it seems that the conduction current in this region can be attributed to the Schottky's effect. The donor level, ϕ, the potential barrier between the metal contact and dielectric material was obtained from the relationship of $\log\left(J_s/T^2\right)$ versus. $1/T$ at the applied field of 170 MV/m (Fig. 10). The obtained donor level was ϕ = 1.37 eV at an applied field of 170 MV/m. Our result are similar to result obtained by P. Karanja and R. Nath [20], who reported ϕ =1.1eV in biaxially-oriented polypropylene

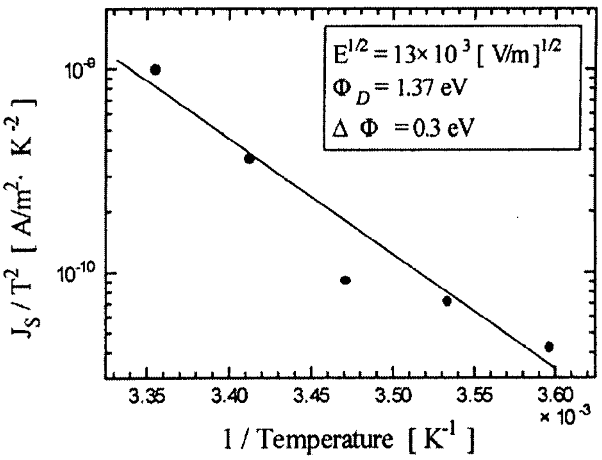


Fig. 10. Plot of J_S/T^2 versus $1/T$ in the Schottky region

3.7. Conduction Mechanism in Region V, E > 190 MV/m.

The increase in conduction current in region V (Fig. 8) is larger than expected from the Schottky effect in region IV. It seems that when the applied field is over 190 MV/m at a temperature 25°C, the current obeys the Fowler-Nordheim relation where current is due to: [10],[21]

$$J_{FN}=A_1E^2\exp\left(-B/E\right) \tag{14}$$

where $A_1=2.2e^3/8\pi h\Phi_D$ and $B=-8\pi d(2m)^{1/2}{\Phi_D}^{3/2}/3he$, m is electron mass and h is Plank's constants. Fig. 11 shows the $\log\left(J_{FN}/E^2\right)$ versus $1/E$ and from the slope the potential barrier Φ_D = 0.3 eV was obtained. Generally, the tunneling current depends strongly on the applied field and is independent of temperature. However, in our experimental results the tunneling current depends on temperature because the carriers first penetrate from the electrode into potential barrier and then the penetrated carriers are released by thermal excitation into the conducting band of the polymer. In other words, both thermionic and field emission occur simultaneously. This results may support the results by M. Ieda and G. Sawa. [22]

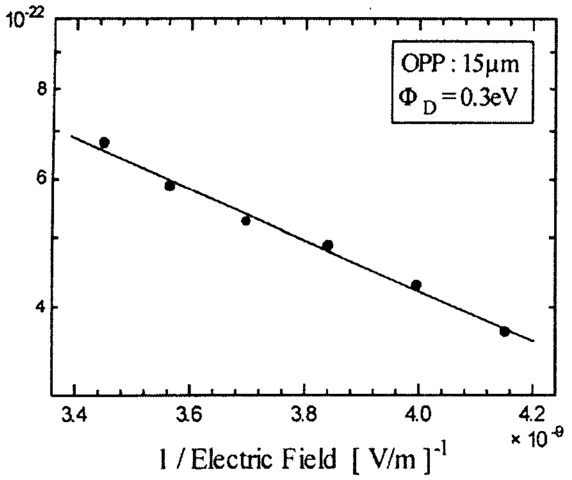


Fig. 11. Plot of J_{FN}/E^2 versus 1/E in the Fowler-Nordheim region

The barrier height in each region may be dominated by the electric field and temperature. Therefore, the conduction mechanism in each region is different.

4. CONCLUSION

The characteristics of the conduction current and current oscillation of OPP films over the electric field from 10 to 300 MV/m and temperature range from 5 to 55°C were obtained. The current-electric field relationship shows nonlinear characteristics, in which five regions can be distinguished. A negative resistance and the periodic current oscillation phenomena were observed at electric fields between 70 and 82 MV/m. The negative resistance characteristics of this region can be explained by Gibbon's theory. The magnitude of the current oscillation goes up with electric field strength and the temperature, but its period decreases with increasing of the applied voltage stress. The mobility of carriers in the negative resistance region was determined to be as 1.44×10^{-13} $m^2/V\cdot s$.

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