Space Charge Limited Currents in Pure and Iodinated Cellulose Acetate Films

ASHOK KUMAR* and RABINDER NATH, *Department of Physics, University of Roorkee, Roorkee-247672, India*

Synopsis

Current as a function of voltage has been studied in pure and iodine doped cellulose acetate in the temperature range 313–373 K. The space charge limited currents (SCLC) have been found to exist in pure and doped samples. The temperature dependence of conductivity is found to correspond to two activation energies. The activation energies calculated from conductivity vs. temperature plots for ohmic and SCLC regions were almost equal showing the extrinsic nature of conduction. The break point at 78°C in conductivity vs temperature plots for pure cellulose acetate may correspond to effective glass transition temperature (T_g'). This has been verified from the differential thermal analysis studies. The effect of iodine doping on the electrical conduction in cellulose acetate has been investigated and the results are reported. The infrared studies reveal that iodine stays in the polymer as a neutral molecule and some of which may interact with the polymer molecules.

INTRODUCTION

During the past few years, there has been considerable interest in the conduction mechanism of organic materials. This interest is a consequence of the hope that organic materials may find use in a wide variety of technological applications. Like many inorganic materials,[1,2] some organic materials[3–6] are also found to exhibit nonlinear current voltage characteristics. This nonohmic behavior can be interpreted on the basis of space charge limited currents (SCLC). The theory of SCLC in insulators is well established and has been a subject of recent reviews.[7,8] The SCLC analysis is quite helpful in calculating a number of important conduction parameters.

In the case of polymers, Turnhout[9] has discussed the existence of trapping centers at various sites. It was observed that the charge carriers are predominantly located in traps and the carrier migration is described by a hopping process in polymers. Previous work has shown that the low value of carrier mobility observed in polymers can be greatly enhanced by impregnating them with iodine.[5,10,11] The iodination of polymers effectively reduces the trapping of charge carriers and makes more carriers available for conduction, thereby enhancing the charge carrier drift in polymers.[5,12]

In the present paper, we report the results of investigations undertaken to identify the conduction mechanism in cellulose acetate. The observed nonlinear behavior of current-voltage measurements is analyzed on the basis of SCLC theory. The effect of iodine doping on the electrical properties of cellulose acetate film is investigated and the results are reported.

* On study leave from Mahamana Malviya College, Khekra, Meerut.

Journal of Applied Polymer Science, Vol. 26, 1787–1794 (1981)
 CCC 0021-8995/81/061787-08$01.00

EXPERIMENTAL

The cellulose acetate having acetic acid content 53.5–56% was used in the present investigations. The films of cellulose acetate and cellulose acetate:-iodine were prepared as follows. The acetone solution of cellulose acetate was poured on to clean glass plate and was kept in acetone atmosphere. This enabled slow evaporation of acetone and resulted in a smooth transparent layer of cellulose acetate. Since the adhesion of cellulose acetate to the glass substrate is poor, the layer was detached easily. The film was heated at 50°C for 12 hr to remove the residual solvent and was cut into 2.1 × 1.4 cm size for experimental investigation. For making the cellulose acetate:iodine layer, iodine (2 wt%) was mixed in the solution and the film was prepared following the process described above. For all samples preparation, the viscosity of cellulose acetate–acetone solution was kept constant to obtain layers of approximately the same thickness, ~15 μm thick.

All the current-voltage measurements were performed on a sandwich cell, using brass electrodes. The steady-state current was registered by ECIL electrometer EA815 after applying the voltage from a highly regulated power supply for 90 min. The observations taken in the temperature range 313–373 K, were reproducible. The temperature was kept constant within an accuracy of ±0.5 K. The dielectric constant measurements were taken employing Marconi Universal Bridge TF 2700 at Frequency 1 kHz.

For taking the infrared spectrum, a Beckman IR 20 Infrared spectrophotometer was used, while differential thermal analysis was performed with a Fisher Differential thermalyzer Model 260, fitted with an automatic voltage stabilizer, recorder, and an amplifier.

RESULTS AND DISCUSSION

The SCLC theory quantitatively describes the experimental current-voltage relationship in the low voltage region ($I \sim U$) and high voltage region ($I \sim U^2$). In the low voltage region, the thermal equilibrium charge density is much greater than space charge density injected into the insulator by ohmic electrodes and current flow is described by Ohm's law

$$I_{\text{ohm}} = neA\mu_o \frac{U}{d} \tag{1}$$

where n is the density of thermally free carriers, e is the elementary charge, μ_o is the free carrier mobility, A is the electrode area, and d is the thickness of the sample.

At sufficiently high voltages, the current is dominated by SCLC which causes a greater current flow and can be written

$$I_{\text{SCL}} = \tfrac{9}{8}\epsilon A\mu_o\theta U^2/d^3 \tag{2}$$

where ϵ is the dielectric constant of the material and θ is the fraction of the total injected carriers that remains free and is given by

$$\theta = \frac{N_c}{N_t} \exp\left(-\frac{E_t}{KT}\right) \tag{3}$$

where N_c is the density of states in the conduction band and N_t represents the

concentration of trapping levels situated at E_t eV below the bottom of conduction band.

Equations (1)–(3) may be used to analyze the experimental current–voltage curve in order to determine the physical observables characterizing electrical conduction.

Figures 1 and 2 show the current–voltage curves for pure and iodine doped cellulose acetate films at various temperatures. Both $I \sim U$ and $I \sim U^2$ regions as predicted by SCLC theory were observed in these samples. In order to confirm that observed currents actually represent SCLC, a study has been made on various pure and iodine doped cellulose acetate films of different thicknesses (Fig. 3). The functional dependence of currents on thickness in SCLC region for pure and iodine doped samples were found to obey the relation $I_{SCL} \propto d^{-3}$, which is in accordance with SCLC theory [eq. (2)].

The steady-state currents, observed in iodine doped cellulose acetate film, were found to be more than in case of pure cellulose acetate film. It indicates that the conductivity of cellulose acetate film increases by iodination. At 50°C, the conductivity of pure cellulose acetate film was found approximately $2.25 \times 10^{-16}\ \Omega^{-1}\ cm^{-1}$, which becomes nearly $3.7 \times 10^{-15}\ \Omega^{-1}\ cm^{-1}$ after doping the film with iodine (2 wt%). The increase in dc conductivity may be explained as follows. The iodine present in the vicinity of the polymer chain behaves as a

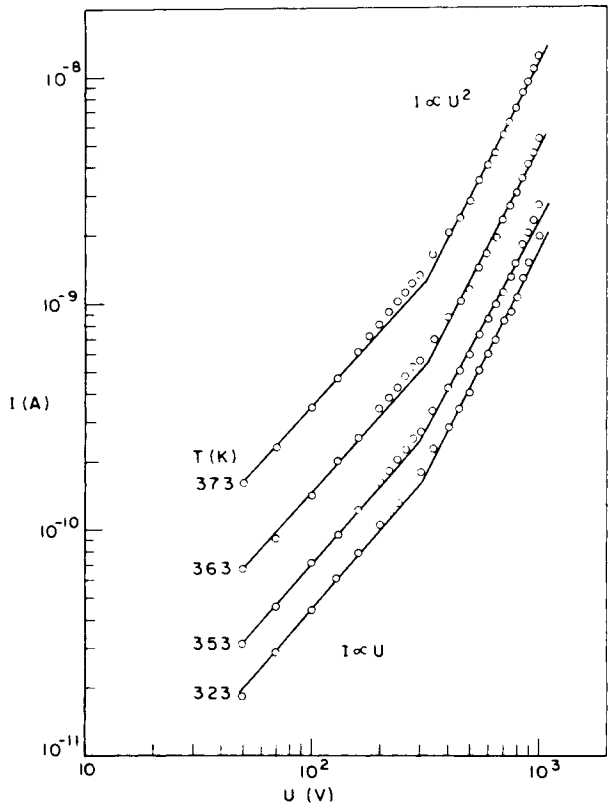

Fig. 1. Current-voltage characteristics of cellulose acetate at various temperatures.

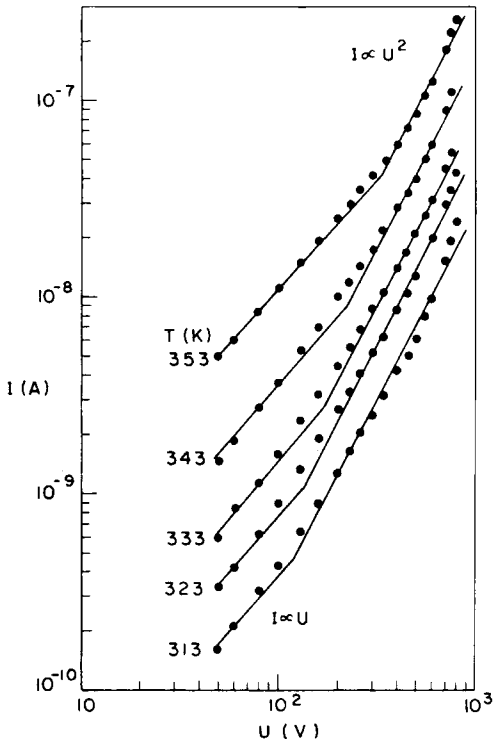

Fig. 2. Current-voltage characteristics of iodine doped cellulose acetate (2% w/w) at different temperatures.

bridge for the transfer of charge carriers from one hopping center to the other, thereby reducing the trapping and thus enhancing the conductivity of sample.

A comparative study of the infrared spectra of pure and iodine doped samples was made and no new peak was observed. However, after iodine doping, infrared spectra of a thin cellulose acetate film showed an increase in the absorption bands at 2850 cm^{-1} (C—H) and 3450 cm^{-1} (O—H) as shown in Figure 4. The increase in absorption at these frequencies may be due to lengthening of C—H and O—H bonds. Probably a weak electrostatic interaction takes place between the iodine and these groups. This interaction results in the deformation of the electron clouds and a lengthening of the mean bond distance of these groups. Therefore, it can be inferred that iodine enters in the polymer as a neutral molecule, some of which interact with the polymer molecules.

A study of temperature dependence of ohmic and nonohmic conductivities is made as it provides the information about the thermal gap between free and bound electron states. Figure 5 shows ln σ vs. T^{-1} curves plotted for pure and iodine doped cellulose acetate films in ohmic and nonohmic regions. These curves indicate different slopes at lower and higher temperatures and therefore different associated thermal activation energy in two regimes. The conductivity curves show the exponential temperature dependence, in both ohmic and SCLC regions. This behavior may be caused by the dependence of n and θ on temperature.[13] The values of thermal activation energy evaluated using the

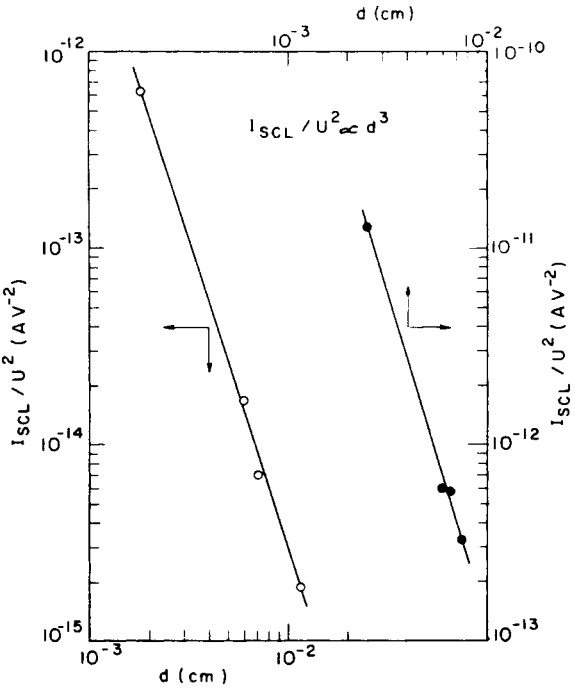

Fig. 3. Thickness dependence of SCL current in pure (○) and 2% iodine doped (●) cellulose acetate.

Arrhenius law for conductivity $\sigma \sim \exp(-E_t/KT)$ at lower and higher temperatures in ohmic and nonohmic regions for both pure and iodine doped samples are found comparable with in the measurement error (Table I). This coincidence will be an indication of the extrinsic nature of dark conduction and in this case the thermal activation energy of dark conduction may be interpreted as the depth of dominant trapping levels.[13]

A comparative study of these activation energies in low and high temperature regions for both samples indicates that in higher temperature range both share in common the value of activation energy. While the activation energy differs markedly in the lower temperature range for both the samples. It shows that iodine doping in cellulose acetate forms a separate trapping level, which is effective in the lower temperature range. The value of the activation energy associated with this new trapping level formed by iodination agrees well with the value obtained previously in iodine.[14]

In the case of many polymers, an effective glass transition, T_g', can be measured from the charge in slope of ln σ vs. T^{-1} plots. Figure 5 exhibits a break point at 78°C in case of pure cellulose acetate. The differential thermal analysis of pure cellulose acetate shows a phase change at about 73°C as shown in Figure 5 (see inset). Hence, this temperature may correspond to an effective glass transition temperature, T_g', of pure cellulose acetate and is in good agreement with the value reported in previous works.[15] After iodine doping this effective glass transition temperature is found to decrease. This decrease in T_g' may be explained on the basis of plasticization effects.[15]

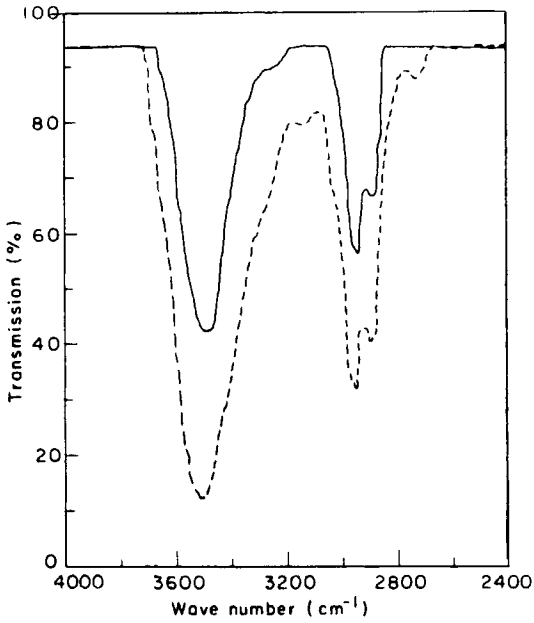

Fig. 4. Infrared spectra of pure (—) and 2% iodine doped (- - -) cellulose acetate.

TABLE I
Values of Activation Energy for Figure 5.

	Activation energy (eV)			
	$T < T_g'$		$T > T_g'$	
Compound	Ohmic region	SCLC region	Ohmic region	SCLC region
Pure cellulose acetate	0.08	0.08	0.90	0.85
Doped cellulose acetate	0.55	0.50	0.90	0.80

Further the values of activation energy observed at higher temperatures, i.e., above T_g' in both the samples were nearly same. While these values were markedly different at lower temperatures, i.e., below T_g'. It reveals that impurity conduction appears below T_g', while the conduction above T_g' is characteristic of the material. The same conclusion was also derived in previous works by Barker et al.,[15] while studying the effect of doping alkali halides in cellulose acetate.

CONCLUSIONS

The SCLC have been observed in pure and iodine doped cellulose acetate films. The temperature dependence of conductivity in these samples may be described by two activation energies. The activation energies evaluated for ohmic and SLCL regions were nearly equal showing the extrinsic nature of conduction mechanism in cellulose acetate films. Differential thermal analysis investigations show that the break point observed in conductivity versus temperature plots

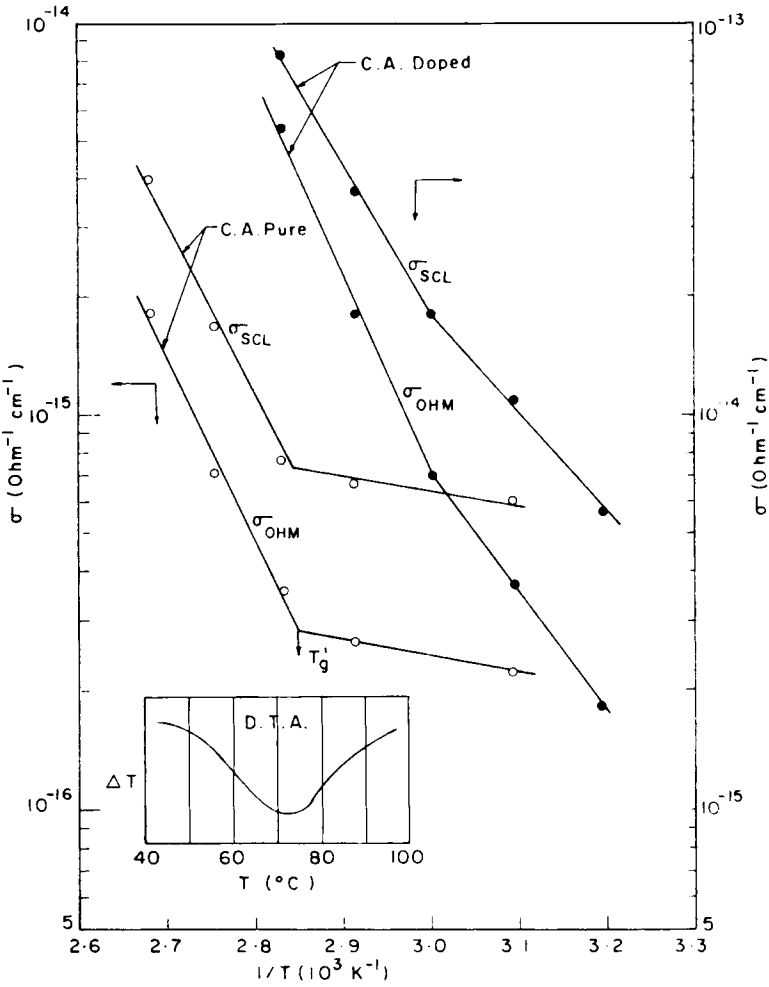

Fig. 5. Temperature dependence of conductivity for pure (○) and doped (●) cellulose acetate (CA) in ohmic and SCLC regions.

may correspond to effective glass transition temperature T_g'. The effect of iodine doping is reflected in low temperature region. The infrared spectra studies reveal the existence of iodine in polymer chain.

The authors are grateful to Professor P. K. C. Pillai of Indian Institute of Technology, Delhi for fruitful discussions. One of the authors (A.K.) acknowledges the financial support of the University Grants Commission of India.

References

1. A. Rizzo, G. Micocci, and A. Tepore, *J. Appl. Phys.*, **48**, 3415 (1977).
2. J. Dresner, M. Campos, and R. A. Moreno, *J. Appl. Phys.*, **44**, 3708 (1973).
3. M. Campos, *Molec. Cryst. Liq. Cryst.*, **18**, 105 (1972).
4. D. G. Shaw and J. W. Kauffman, *Phys. Stat. Solidi* (*a*), **4**, 467 (1971).
5. A. Kumar and R. Nath, *Phys. Stat. Solidi* (*a*), to appear.
6. A. S. Siddiqui and E. G. Wilson, *J. Phys. C: Solid State Phys.*, **12**, 4237 (1979).
7. M. A. Lampert and P. Mark, *Current Injection in Solids*, Academic, New York, 1970.

8. R. M. Hill, *Thin Solid Films.* **15,** 369 (1973).
9. J. V. Turnhout, Ph.D. Thesis, University of Leiden, Holland (1972).
10. D. K. Davies and P. J. Lock, *J. Electrochem. Soc.*, **120,** 266 (1973).
11. W. D. Gill, *Energy and Charge Transfer in Organic Semiconductors*, K. Masuda and M. Silver, Ed., Plenum, New York, 1974, p. 135.
12. D. K. Davies, *J. Phys. D: Appl. Phys.*, **5,** 162 (1977).
13. G. G. Robert and F. W. Schmidlin, *Phys. Rev.*, **180,** 785 (1969).
14. A. Many, S. Z. Weisz, and M. Simhony, *Phys. Rev.*, **126,** 1989 (1962).
15. R. E. Barker, Jr. and C. R. Thomas, *J. Appl. Phys.*, **33,** 87 (1964).

Received September 24, 1980
Accepted December 18, 1980